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# Demonstration/Validation of the Snap Sampler Passive Ground Water Sampling Device for Sampling Inorganic Analytes at the Former Pease Air Force Base

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# Demonstration/Validation of the Snap Sampler Passive Ground Water Sampling Device for Sampling Inorganic Analytes at the Former Pease Air Force Base

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**Abstract:** Laboratory studies and a field demonstration were conducted to determine the ability of the Snap Sampler to recover representative concentrations of several types of inorganic analytes from ground water. Analytes included non-metals, transition metals, alkaline earth metals, alkali metals, and a metalloid. In the laboratory studies, concentrations of analytes in Snap Sampler samples were com-parable with concentrations of the analytes in samples collected from a standpipe (i.e., control samples). For the field demonstration, there were sampling events at the former Pease Air Force Base. Samples taken using a Snap Sampler were compared with samples collected using conventional low-flow purging and sampling and a regenerated cellulose passive diffusion sampler. Based upon statistical analyses, analyte concentrations were found to be equivalent to those in the low-flow samples with one exception – unfiltered iron, where concentrations were significantly higher in the Snap Sampler samples. Differences were most pronounced in samples collected from the two stainless steel wells and from wells with higher turbidity levels. Elevated turbidities may have resulted from installing additional sampling equipment (including the baffle, pump, samplers, and bottom weight) in the well before sampling. We will examine this issue further at our next test site.

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# **Preface**

This report was prepared by the U.S. Army Engineer Research and Development Center (ERDC) — Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, New Hampshire. Funding was provided by the Environmental Security Technology Certification Program (ESTCP) under Project ER-0630: "Demonstration/Validation of the Snap Sampler Passive Ground Water Sampling Device" with Dr. Andrea Leeson as Program Manager for Environmental Restoration.

This report was prepared by Louise V. Parker and Nate Mulherin, Biogeochemical Sciences Branch, and Gordon Gooch, Engineering Resources Branch, at ERDC-CRREL.

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This report was prepared under the general supervision of Dr. Terrence M. Sobecki, Chief, Biogeochemical Sciences Branch; Dr. Thomas J. Tantillo, Chief, Engineering Resources Branch; and Dr. Justin B. Berman, Chief, Research and Engineering Division. Branch.

At the time of publication, Dr. Lance D. Hansen was Deputy Director and Dr. Robert E. Davis was Director, CRREL.

COL Gary E. Johnston was the Commander of ERDC and the Director was Dr. James R. Houston.

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<sup>&</sup>lt;sup>1</sup> Pease International Tradeport is located on the site of the former Pease Air Force Base.

# **Executive Summary**

This report was completed as a partial fulfillment of the obligations established for ESTCP Demonstration Project ER-0630. The objectives of this project were to demonstrate that the Snap Sampler passive ground water sampling device can provide (1) technically defensible analytical data for the wide spectrum of analytes that are of concern to the Department of Defense (DoD) and (2) offer substantial cost savings in the process. Our research plan was to use this device to collect samples at five sites, for a range of analyte types including: VOCs, explosives, perchlorates, metals, and natural attenuation parameters. The demonstration for this project was conducted at the former Pease Air Force Base in Portsmouth, NH. The analytes of interest were several metals (including two alkali metals, two alkaline-earth metals, and two transition metals) and one metalloid (arsenic).

Prior to conducting this field study, two laboratory studies were conducted to determine the ability of the Snap Sampler to recover representative concentrations of several inorganic analytes including non-metals (bromide, chloride, nitrate, perchlorate, and sulfate); a metalloid (As), and several metals including alkali metals (sodium [Na] and potassium [K]); alkaline earth metals (magnesium [Mg] and calcium [Ca]); and transition metals (cadmium [Cd], chromium [Cr], manganese [Mg], and iron [Fe]). For these studies, concentrations of analytes in samples taken with the Snap Sampler were compared with known concentrations of the analytes in samples collected from a standpipe (i.e., control samples). These studies clearly demonstrated that the Snap Sampler recovered equivalent concentrations of the inorganic analytes used in these studies, when compared with the control samples.

For the field demonstration, there were 10 sampling events. Inorganic analytes that were found at concentrations above the detection limit at this site included: As, Ca, Fe, Mg, Mn, K, and Na. Analyte concentrations in samples collected with the Snap Sampler were compared with samples collected using the EPA's low-flow purging and sampling protocol (U.S. EPA Region 1 1996). Both filtered and unfiltered samples were analyzed. Samples were also collected using a Regenerated Cellulose (RGC) passive diffusion sampler and concentrations in these samples were compared as

well. Using these three sampling technologies allowed us to compare dissolved and colloid-borne contaminants.

This demonstration showed that the Snap Sampler recovered equivalent concentrations of most inorganic analytes, compared to those obtained by using the EPA's low-flow purging and sampling protocol; the exception to this was unfiltered (total) iron where concentrations were higher in the Snap Sampler. Concentrations of unfiltered iron were especially higher in the two stainless steel wells and appear to reflect the turbidity levels in the wells at the time of sampling. Elevated turbidities may have been an artifact of the experimental design that resulted from installing the baffle and additional sampling equipment (including the pump, and RGC and Snap samplers) in the well before sampling. However, because deploying several Snap Sampler bottles in a well may also elevate turbidity in the well, future studies should examine this issue in more depth. Therefore we concluded that for most inorganic analytes, this sampler appears to be a viable alternative to low-flow sampling at this site.

While the RGC sampler can only provide filtered samples, analyte concentrations in these samples were equivalent to those found in the unfiltered low-flow samples. The use of the RGC sampler in conjunction with low-flow sampling and the Snap Sampler demonstrated that colloidal transport of these analytes was not predominant at this site.

Other primary performance criteria used to evaluate the Snap Sampler and RGC sampler included reduced sampling time and/or reduced personnel requirements, ease of use, minimal training required, reduced purge water, sample performance, and sampler reliability. Clearly, both passive methods resulted in reduced personnel requirements (one person could easily sample a well vs. the two typically used for low-flow sampling) and a reduced sampling time (or more wells sampled per day). The RGC sampler was the easiest to use. We found that the Snap Sampler required some training and experience before one could operate the sampler without error. This was especially true with respect to learning to assemble the sampler. Since neither passive sampling method involves purging the well, there is no purge water to dispose of with either method. However, there was a small amount of spent sample to dispose of with use of the RGC sampler.

Generally, the Snap Samplers performed well by triggering on demand and by providing full samples. Although, there were a few instances where one of the caps did not seal properly because an o-ring did not seat properly and there was some loss of sample in those cases. Also, there were a couple of bottles that had pinhole leaks in the seam, which resulted in losses of sample during shipping and storage. As a result of this issue, the manufacturer has switched to a different polymer that has better weld properties. Because of the issues with the o-rings, we would recommend that an additional Snap Sampler bottle be added to the trigger line as insurance. In contrast, we did not observe any issues with the RGC samplers.

While there were no injuries related to using any of the three sampling technologies, the general consensus was that there are far fewer safety issues associated with using the passive samplers vs. low-flow sampling and all the paraphernalia associated with its use (including a generator, electrical cords, gasoline, etc.).

The long-term costs associated with using these methods were calculated based on the costs of this demonstration. The projected long-term costs were determined for a similar site with 50 wells where quarterly sampling is conducted over 10 years. Based on these calculations, the Snap Sampler can provide a 67% cost savings vs. using low-flow sampling. If there is only a need to analyze for dissolved species of metals, the RGC sampler could provide a cost savings of 71%. We estimated that the average cost per sample was \$187.70, using low-flow sampling at this site over 10 years; the similar cost per sample for the Snap Sampler was \$62.40, and for the RGC sampler was \$53.95 (without factoring inflation into these costs).

The primary cost drivers for this technology are: the number of analytes and sample volume requirements, depth of the sampling interval, and whether the wells would require reconditioning. However, even if one had to recondition the wells every 5 years and was sampling for a large number of analyte types, our cost analyses indicated this technology can still provide substantial cost savings over low-flow purging and sampling.

We believe this demonstration showed that, when compared to low-flow purging and sampling methods, the Snap Sampler: (1) recovered comparable concentrations of several types of inorganic analytes, (2) offered fewer safety concerns, (3) took considerably less time and manpower to collect samples, and (4) was considerably less expensive than low-flow sampling. The primary limitations with this technology were: (1) it may not be suitable for collecting samples to be analyzed for total Fe (and possibly other reactive species), if placing the sampler in the well disturbs the well and elevates turbidity and oxygen levels in the well, (2) it took longer to learn how to collect samples than with a diffusion sampler such as the RGC sampler, and (3) there were issues with sealing a small percentage of the bottles. We will be examining the first issue in subsequent studies.

If one is only interested in determining the dissolved concentrations of these analytes, the RGC sampler is also an economic alternative for sampling for inorganic analytes.

# **Unit Conversion Factors**

Multiply	Ву	To Obtain
acres	4,046.873	square meters
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
fathoms	1.8288	meters
feet	0.3048	meters
gallons (U.S. liquid)	3.785412 E-03	cubic meters
horsepower (550 foot-pounds force per second)	745.6999	watts
inches	0.0254	meters
inch-pounds (force)	0.1129848	newton meters
miles (U.S. statute)	1,609.347	meters
miles per hour	0.44704	meters per second
mils	0.0254	millimeters
ounces (mass)	0.02834952	kilograms
ounces (U.S. fluid)	2.957353 E-05	cubic meters
pints (U.S. liquid)	4.73176 E-04	cubic meters
pints (U.S. liquid)	0.473176	liters

# 1 Introduction

## 1.1 Background

Low-flow purging and sampling methods currently in use (Puls and Barcelona 1996; U.S. EPA Region 1 1996; Nielsen and Nielsen 2002; ASTM 2003) are expensive because of the time involved in waiting for purge parameters to stabilize, the capital cost of the dedicated equipment (pumps or costly decontamination of the equipment between sampling events), and in many instances, the costs associated with disposing of the purge water. Low-flow sampling also causes extensive mixing within the well and well bore, and this prevents vertical profiling of the contaminant plume. One recent estimate places the monitoring costs for the U.S. Army for the next 10 years at almost \$500 million.<sup>2</sup> Given both the issues of concern and the staggering costs associated with long-term monitoring, finding a sampling method that is less labor-intensive and less costly (but able to yield quality data), is clearly needed.

Passive sampling techniques are gaining acceptance in the scientific community for many ground water sampling applications (ITRC 2004, 2006, 2007; NJDEP 2004). Passive sampling techniques rely on the continuous natural flow through the well screens (Robin and Gillham 1987; Powell and Puls 1993; ASTM 2003). Where the use of passive sampling is appropriate, data-quality improvements and cost reductions include: better delineation of contamination with depth within the screened zone, reduced volumes of purge water waste, reduced labor during sampling, and reduced equipment costs. Parsons (2003) estimated that the potential cost-savings using passive techniques for long-term monitoring at Department of Defense (DoD) facilities is on the order of 70%, compared to low-flow ground water sampling.

Although the improvements and potential cost savings associated with passive sampling are significant, most passive sampling devices have limitations. For example, the Polyethylene Diffusion Bag (PDB) sampler can be used only for selected volatile organic compounds (VOCs), and while the Regenerated-Cellulose Dialysis sampler (or RGC sampler) can be used for a broader range of contaminants, there are concerns about the

<sup>&</sup>lt;sup>2</sup> www.denix.osd.mil/denix/DOD/Policy/Army/Aerta/tnstop.html

length of time this sampler can be deployed before it starts to undergo biodegradation. Also, because diffusion samplers typically require at least several days for equilibration to occur, they yield a concentration that is a time-weighted average (as compared with samples that are collected in "real time"). In comparison, equilibrated grab-type samplers (such as the HydraSleeve and Snap Samplers) can be used to obtain whole water samples in real time for any type of analyte. These devices are deployed in the well and left to allow time for the well to recover and for the materials to equilibrate with the analytes in the well water prior to collecting a sample. However, unlike the HydraSleeve sampler, the Snap Sampler has an advantage in that the sample is collected and sealed under *in-situ* conditions, and can remain sealed until the sample is analyzed. There is little or no agitation of the water column as the sample is collected, and no chance of accidentally recovering any of the stagnant water above the well screen as the device is brought to the surface.

### 1.2 Objectives of the demonstration

The objectives of this demonstration/validation project were to demonstrate that the Snap Sampler passive ground water sampling device can provide (1) technically defensible analytical data for the wide spectrum of analytes that are of concern to the DoD and (2) substantial cost savings. A third objective was to facilitate technology transfer and acceptance of this sampling method. The Snap Sampler is an equilibrated grab sampler (ITRC 2006, 2007) that allows one to collect a whole water sample under *in-situ* conditions without agitating the well during sample collection. Once samples are collected, they can remain in the sampling bottle and do not require additional transfer to another container, thereby reducing the possibility of loss of volatiles, reaction of analytes with the air during transfer, or contamination by the air.

Our demonstration plan was to collect samples at five sites with three sampling technologies: (1) the Snap Sampler, (2) low-flow purging and sampling (U.S. EPA Region 1 1996), and (3) wherever applicable, passive diffusion samplers such as the RGC sampler, PDB sampler, or Rigid Porous Polyethylene (RPP) sampler. Analytes to be included in this demonstration include VOCs, explosives, perchlorate, metals, and natural attenuation parameters. Using these three sampling technologies will allow comparison of dissolved and colloid-borne contaminants (such as metals, and the more hydrophobic organic contaminants, including explosives).

This particular demonstration took place at the former Pease Air Force Base (AFB) site near Portsmouth, New Hampshire. Inorganic analytes found at detectable levels at this site included one metalloid (As), and several types of metals including alkaline metals (Na and K), alkaline earth metals (Ca and Mg), and transition metals (Mn and Fe). Analyte concentrations in samples taken with the Snap Sampler were compared with those taken using low-flow sampling, and the RGC passive diffusion sampler. Both filtered and unfiltered samples were compared.

#### 1.3 Regulatory drivers

Currently, the preferred method for sampling a ground water monitoring well is to use a low-flow purging and sampling method as first outlined by Puls and Barcelona (1996) and now promulgated by others, including the U.S. EPA Region 1 (1996), Nielsen and Nielsen (2002), and the ASTM (2003). However, because low-flow sampling draws water most heavily from the most permeable part of the formation (which may not be the zone of interest), does not allow vertical profiling of the contaminants in the well or plume, and is both time consuming and expensive, finding a sampling method that is less labor-intensive and costly (but able to yield quality data) is clearly needed.

## 1.4 Stakeholder/end-user issues

Many concerns from stakeholders, regulators, and end-users have been addressed by the Interstate Technology and Regulatory Council (ITRC) Passive Sampler team. This team published a protocol document on the use of five passive samplers that includes the Snap Sampler. This document is available free at the ITRC website (ITRC 2007). This document serves as a guide to regulators, technology users, and stakeholders on how to properly deploy and collect samples using this technology. In addition, ITRC has offered free Internet training to any interested party including stakeholders, regulators, and end-users.

# 2 Technology Description

## 2.1 Technology development and application

While most previous research and development of passive ground water samplers has focused on diffusion-based devices, the Snap Sampler (Figure 1) is a grab-type device that was initially developed by Sanford Britt of ProHydro, Inc. to improve data quality of VOCs. Specifically, the initial objectives were: (1) to collect a sample at discrete levels that would allow profiling contamination with depth within the well, (2) to reduce inconsistencies associated with the sampling methods and personnel, and (3) to reduce losses during sample transfer. However, the applicability of this device to a broad spectrum of analytes was evident immediately because this sampler can collect a whole water sample under *in-situ* conditions without agitating the well during sample collection and can be used to sample any of the analytes of concern to the DoD. Typically, after these samplers are deployed, the well is then left and given time to re-equilibrate with the natural formation water flowing through the well.

The Snap Sampler consists of the sampler body that holds the sample bottle in place, a sample bottle that is open on both ends, and a trigger line with a trigger. The device is deployed so that both ends of the sample bottle are open, and the trigger releases spring-activated end caps that seal the bottle. The trigger line is attached to a well docking station during deployment ensuring that the sampler remains at the desired depth in the well. Components of the plastic Snap Sampler and its deployment are shown in Figure 1. (If preferred, stainless steel sampler bodies can also be purchased for the Snap Sampler.) This sampler is different from most others in that samples remain in the sampling bottle and do not require additional transfer to another container after they are recovered from the well. During transfer, this feature reduces the possibility of loss of volatiles or reaction of the analytes with the air. Currently, available sampling bottle options include 40-mL glass volatile organic analyte (VOA) vials, 125-mL high-density polyethylene (HDPE), and 350-mL HDPE bottles. The 350mL bottle fits into 4-in. diameter wells (and larger). The VOA vials and the 125-ml bottles fit into 2-in. diameter wells (or larger). The VOA vials can be used in common laboratory autosampler equipment. Multiple bottles can be deployed in tandem on a single trigger line, or on multiple trigger lines when different types of samples need to be collected or when larger

sample volumes are required. Up to four Snap Samplers can be deployed in tandem on a single mechanical trigger line. For deep wells, an electronic activator or a pneumatic activator can be used to trigger the samplers. These devices allow one to deploy five or six samplers on a single line.

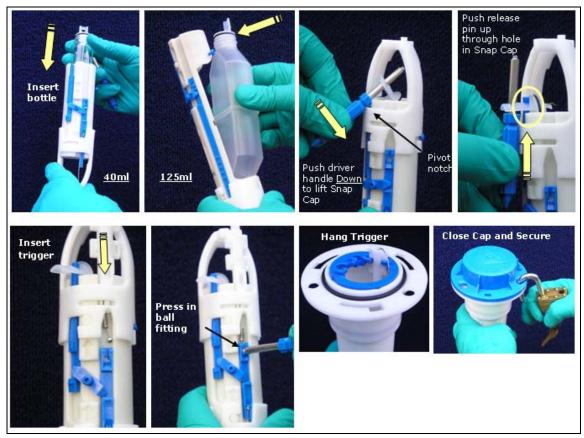


Figure 1. Snap Sampler deployment procedure.

## 2.2 Previous testing of the technology

#### 2.2.1 Proof of concept: Laboratory tests

Under the sponsorship of the U.S. Army Corps of Engineers (USACE) Long-Term Monitoring (LTM) Program, Parker and Mulherin (2007) examined the ability of the Snap Sampler to recover representative concentrations of VOCs and explosives, under laboratory conditions and in a limited number of field trials. For the laboratory studies, sampling was conducted in an 8-ft high (8-in. diameter) standpipe that contained known concentrations of a suite of either VOCs or explosives. The samplers were deployed at the same depth as the sampling port on the standpipe, and analyte concentrations in the Snap Sampler samples were compared with

the concentrations of the various analytes in the control samples collected from the standpipe's sampling spigot.

For the initial studies, the Snap Samplers were left for 24 hours to allow time for the materials in the sampler to equilibrate with the test solution. The two test solutions contained either 7 VOCs or 6 explosives, measured at ppm- and ppb-levels. For all the analytes tested, statistical analyses (paired-t tests at 95% confidence level) revealed that there was no significant difference between the mean concentrations of the analytes in the Snap Samplers vs. the controls. The data from these studies can be found in Appendix Table F1 and Table F2.

For the previous studies, the samples were analyzed within 24 hours. However for most sampling events, samples are typically shipped to a laboratory and held for several days (or longer) prior to analyses. Given that the Snap Sampler contains a Teflon-coated spring and two Teflon-coated end caps, it is possible there could be significant sorption of the analytes by these materials if the equilibration period was not long enough (Parker and Ranney 1994, 1997, 1998, 2000; Ranney and Parker 1998a). To address this concern, several follow-up studies were conducted to determine if there were additional analyte losses when the samples reached their maximum holding times. For samples containing explosives, typically no preservative is added and the maximum holding time is 7 days. For VOC samples, the maximum holding time is 7 days if the samples are not preserved or 14 days if they are preserved. These studies are summarized below and data are summarized in Appendix Table F3 for the VOCs and Appendix Table F4 for the explosives.

The Snap Samplers were deployed in the standpipe containing the test solution and left to equilibrate for 24 hours, as described in the previous experiments. After collecting the samples, the bottles (for explosives) or vials (for VOCs) were then held for the prescribed maximum holding times. For the VOCs, vials with and without preservative were tested. We found that representative concentrations of explosives could be recovered from the (unpreserved) samples containing explosives after holding the samples for 7 days. However, when this sampler was used to sample VOCs, we found statistically significant losses of VOCs in both the preserved samples (14-day holding time) and the unpreserved samples (7-day holding time). For the unpreserved samples, differences in the mean concentrations for the analytes ranged from no loss to a 61% loss. For samples that were pre-

served but were held for the full 14-day holding time, the mean losses were not as large, with a maximum loss of 36%. One possible explanation for the observed losses was that a longer equilibration time (greater than 24 hours) is needed.

Two additional holding time studies for the VOCs were then conducted. These studies were similar in design except that the equilibration period was 3 days (rather than 24 hours). For the unpreserved samples, differences were relatively small (< 5%) for all the analytes except *m*-xylene (mXYL). For the preserved samples, differences were also relatively small (<5%) for all the analytes except mXYL. For mXYL, the mean loss was substantially less than that found in the previous study (with a 24-hr equilibration period) but was still substantial (e.g., the preserved samples loss was 23 % vs. 36% in the previous study). Therefore, it appears that 3 days is sufficient equilibration time for VOCs, with the possible exception of mXYL.

There have not been any laboratory studies that have examined the ability of the Snap Sampler to recover inorganic analytes. So prior to any field work, this demonstration included plans to test the ability of the Snap Sampler to recover representative concentrations of several types of metals and other inorganic ions in laboratory studies. The results from these studies are given later.

#### 2.2.2 Previous field tests

Parker and Mulherin (2007) conducted limited field trials of the Snap Sampler for VOCs and explosives at three locations. Specifically, the Cold Regions Research and Engineering Laboratory (CRREL) site (Hanover, NH) contained trichloroethylene (TCE); the Silresim Superfund Site (Lowell, MA) contained benzene, toluene, ethylbenzene, and xylene (BTEX) compounds and several chlorinated VOCs; and the former Louisiana Army Ammunition Plant (Minden, LA) contained several explosives and daughter compounds, including trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX). Concentrations of the analytes in samples collected with the Snap Sampler were compared with those collected using the EPA's low-flow purging and sampling method. Statistical analyses revealed no significant differences that could be associated with the sampling method for either the VOCs or explosives.

Other field studies include one conducted by Britt, Parker, and Cherry that is currently in review. Another was conducted at the former McClellan Air Force Base (Parsons 2005). Although the McClellan AFB study has not been published in a peer-reviewed journal, the final report is available at the manufacturer's Web site.<sup>3</sup>

In the Parsons (2005) study, 6 different passive samplers (including the Snap Sampler), were compared with both a low-flow purging and sampling method and a well-volume purging and sampling method (i.e., the well was purged of 3-5 well volumes, and then a sample was collected using a bailer). For the Snap Sampler, concentrations of VOCs (including 1,4dioxane) and anions were compared. Unfortunately, interpreting the results from this study is difficult. This is due in part to the different methods used, both in sampling and sample handling (including different sampling times and compositing the VOC samples for the other passive sampling methods), the numerous methods that were used to analyze the data, and issues with some of statistical analyses (e.g., the data was pooled for the various analytes prior to conducting the statistical analyses). However, regression plots of the (pooled) VOC data were informative. These plots showed that the Snap Sampler VOC concentrations correlated well with those taken using low-flow sampling (r2 = 0.995), but were substantially higher (the slope was 1.77). While we might expect these results based on the differences in handling these samples, it is interesting that the concentrations in the samples collected using the well-volume purge method were equivalent to those in the Snap Sampler (r2 = 0.90 with a slope of 1.04). Findings were similar for Snap Sampler concentrations of the anions and 1,4-dioxane, although the slope (1.2) was considerably closer to 1.0.

# 2.3 Factors affecting cost and performance

For this demonstration, the performance of the Snap Sampler was evaluated by comparing analyte concentrations in samples taken using low-flow sampling, the Snap Sampler, and the RGC sampler. Subjective measures such as user-reported ease of use and time to proficiency were also used to determine the over-all performance of the Snap Sampler.

With respect to the performance of the sampler (i.e., its ability to recover a representative sample), various factors can impact the composition of a

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<sup>&</sup>lt;sup>3</sup> http://www.snapsampler.com/images/McClellan\_Report\_Highlighted.pdf

ground water sample and therefore the sampler's performance. These factors include the hydrogeology of the site, well construction, well development, and the experience of the field personnel. Different sampling methods may yield different results depending upon these factors. Performance of the various sampling methods may also vary depending upon analyte type, and weather may impact the performance of sampling devices (especially on hot, sunny days). Although low-flow purging and sampling is currently the industry standard, there is currently no sampling method that yields the "correct" result. Therefore, when interpreting the data from this demonstration or similar studies, it is important to understand conceptual differences of each sampling technology and the site hydrogeology.

As for cost, factors such as the initial equipment costs (including any necessary ancillary equipment such as generators, air compressors, etc.), sampling time and personnel requirements, decontamination, and waste disposal clearly affect total cost. Major operating costs consist of the field crew's salary (time) and occasionally, travel costs. For the Snap Sampler, the device's ease of use, the familiarity of the sampling person with the device, and the total sampling time will impact cost.

## 2.4 Advantages and limitations of the technology

Advantages associated with using the Snap Sampler include that it collects a whole water sample under *in-situ* conditions, does not agitate the well during sample collection, can be used to collect a sample at a discrete depth in the well, and can be used to sample a broad spectrum of analyte types. In addition, samples do not require additional transfer to another container after collection, there is no purge water generated that requires disposal, and there are no power requirements for this sampler. Because samples remain in the original bottle they were collected in, presumably there is a reduced chance for losses of volatiles or changes in concentrations of dissolved gases or analytes subject to oxidation/precipitation reactions (that can occur during transfer). Data uncertainty due to variability in sampling technique (associated with different personnel), hot and/or sunny weather, and exposure to the atmosphere (and any airborne contaminants) also are presumably reduced.

While the HydraSleeve<sup>4</sup> is similar in many respects (i.e., it can be used to collect a whole water sample, it can be used to sample for any type of analyte), the samples are not necessarily collected at a discrete depth in the well but rather over an interval that is ~ 1.5 times the length of the sampler. Also, although the reed valve on the HydraSleeve closes once the sampler is full, the Snap Sampler bottle is sealed tightly at the sampling depth, and there is no need to transfer the sample at the well head with the Snap Sampler as there is with a HydraSleeve sampler.

Because the Snap Sampler is deployed prior to sampling (to allow the well to recover from any disturbance associated with placing it in the well), and because this device collects a whole water sample instantaneously, presumably samples collected with this sampler should not have elevated turbidity (i.e., soil-derived, non-transportable particles) and thus would reflect the true, naturally mobile, colloid-borne contaminants flowing through the well. In contrast, even low-flow sampling has been shown to artificially elevate particle levels in some wells (Bailey et al. 2005), and most diffusion samplers cannot collect colloidal particles because of the small pore sizes of the membranes.

Previous studies by CRREL (Parker and Ranney 1998) have demonstrated that when low-flow purging and sampling is used, sorption by longer lengths of polymer tubing can substantially reduce concentrations of some VOCs. In contrast, there were no losses of these analytes in samples where the Snap Sampler was equilibrated prior to collecting the sample (Parker and Mulherin 2007). However, one of the primary distinctions between low-flow purging and sampling, and using the Snap Sampler, is that the Snap Sampler can be used to collect a sample at a discrete depth in the well, whereas the low-flowing sampling collects a sample that is a flow-weighted average over the entire screen.

One final advantage associated with using the Snap Sampler is that it can be used to sample wells with slow recharge. This is also true for other passive (no-purge) samplers whether they are a diffusion sampler (e.g., the PDB sampler), a sorptive sampler (e.g., the Gore Module) or another grabtype device (e.g., the HydraSleeve). In contrast, any purging method that removes all the water from the well will yield suspect samples for volatiles and analytes subject to oxidation/precipitation reactions.

<sup>4</sup> The HydraSleeve is a disposable, passive, no-purge, ground-water sampler that was developed and is manufactured by GeoInsight of Las Cruces, NM.

The principle limitations with this technology are well diameter and sample volume. The Snap Sampler does not fit into wells with diameters smaller than 2 in. While this sampler can be used to sample for any type of analyte, including those parameters typically measured during purging when collecting low-flow samples, analyses of multiple analyte types and QA/QC samples increase sample volume requirements. Sample volume can be increased by using multiple samplers, either on multiple trigger lines or in tandem on the same trigger line. Up to four samplers can be deployed in tandem on the same trigger line (using a conventional trigger line), and five to six samplers can be deployed on lines using an electronic trigger or a pneumatic trigger. Also, in many cases, sample volume requirements can be reduced by working closely with the analytical laboratory. With time, sample volume is expected to become less of an issue for these samplers, as analytical methods improve.

While the volume of samples collected using low-flow purging and sampling typically is not limited (as long as there is adequate flow in the well), several other passive samplers also have similar volume limitations (especially the Rigid Porous Polyethylene [RPP] sampler). Again, multiple samplers can be deployed to circumvent this problem, and some samplers (e.g., the RGC sampler and the HydraSleeve sampler) can be made in longer lengths, to accommodate larger sample volume requirements.

# 3 Demonstration Design

## 3.1 Performance objectives

The performance objectives are outlined in Table 1 and include qualitative as well as quantitative measures of performance. Specifically, ease of use, reduced sampling time, ability to sample a range of analyte types and concentrations, agreement between analyte concentrations, and a lack of bias associated with the passive samplers were noted.

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance Objective Met?
	1. Ease of use	Little training required	Required training & some repetition for smooth operation
Qualitative	2.Ease of use	Few problems requiring second attempt to sample well	Yes
	3. Faster sampling	Less time needed to sample a well	Yes
	4. Ease of Use	Operator acceptance	Yes
	Agreement between sampling methods for analytes of interest	Lack of statistically significant differences	Yes, with one exception
Quantitativo	2. Lack of bias with sampling method	Statistically significant correlations	Yes
Quantitative	3. Ability to sample a range of contaminants at site	Adequate sample volume for all analyses	Yes
	4. Ability to sample a range of analyte concentrations	Equivalent sensitivity for methods	Yes

Table 1. Performance objectives

## 3.2 Selecting test site(s)

The initial three requirements for a test site were that it (1) contain a variety of inorganic analytes, (2) be within an easy driving distance from our laboratory (since this would be our first demonstration), and (3) have larger diameter ( $\geq 4$  in.) wells. Richard Willey (U.S. EPA Region 1) and Ms. Parker (CRREL) examined EPA databases for New England sites contaminated with metals and metalloids. Subsequent screening included five additional criteria: (1) the wells were monitoring wells (vs. injection and recovery wells used in remediation), (2) the wells met American Society for

Testing and Materials (ASTM) design criteria, (3) the wells had concentrations at least three times the detection limit for one or more analytes, (4) there be at least five wells that met these criteria, and (5) there be no free product in the wells. After some searching, we found that the former Pease AFB met all the test site qualifications.

#### 3.3 Test site description

The former Pease AFB occupies approximately 4,365 acres and is located on a peninsula in southeastern New Hampshire (Figure 2). The former AFB is located in the town of Newington and the City of Portsmouth. The peninsula is bounded on the west and southwest by Great Bay, on the northwest by Little Bay, and on the north and northeast by the Piscataqua River.

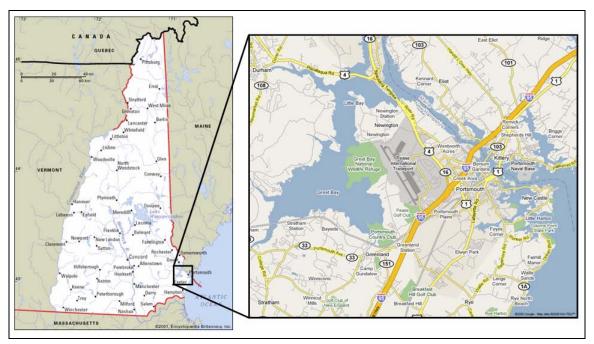


Figure 2. Map of the state of New Hampshire showing the location of the former Pease AFB.

At the onset of World War II, the U.S. Navy used this location as an airport. The Air Force assumed control of the site in 1951, and construction of the base was completed in 1956. Over time, various quantities of fuels, oils, lubricants, solvents, and protective coatings were used, and as a result, contaminants from these substances were released into the environment. Specifically, fuels, organic solvents, polycyclic aromatic hydrocarbons (PAHs), and metals have been found in soils on the base. The ground water has been found to be contaminated with volatile organic compounds

(VOCs) including trichloroethylene (TCE) and tetrachloroethylene (PCE). PAHs, pesticides, and heavy metals have been found in the sediments from various discharge ditches.

In 1976, the DoD conducted an assessment of the environmental contamination resulting from the past operation and disposal practices. In 1984, a Phase I Problem Identification Search was completed, and the Air Force was designated as the lead agency authority to conduct Comprehensive Environment Response, Compensation and Liability Act (CERCLA)<sup>5</sup> cleanup activities.

In December 1988, Pease AFB was selected for closure as a result of the Secretary of Defense's Base Realignment and Closure (BRAC) Commission. The base was closed as an active installation in March 1991, and the Air Force has transferred most of the property to the Pease Development Authority. The airfield is now a fully operational commercial airport. Other property is currently being used or developed for light commercial and industrial facilities. A portion of the base was transferred to the U.S. Department of Interior for use as a national wildlife refuge, and the Air Force retained 229 acres of the former base for use by the New Hampshire Air National Guard.

The former AFB was listed on the EPA's National Priorities List (NPL) in 1990. In 1991, the Air Force, EPA, and New Hampshire Department of Environmental Services (NHDES) signed a Federal Facility Agreement (FFA), establishing the protocols for conducting the environmental study and cleanup of the former AFB. This agreement established eight Installation Restoration Plan (IRP) zones, for which separate remedial investigation and feasibility study (RI/FS) reports were prepared (Figure 3).

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<sup>&</sup>lt;sup>5</sup> CERCLA is commonly known as the Superfund and was enacted in 1980 by the U.S. Congress.



Figure 3. Map outlining IRP zones at the former Pease AFB (from MWH Americas, Inc. 2004).

The eight monitoring wells selected for this demonstration are located in Zones 1 and 3. Zone 1 is located in the eastern part of the former base; Zone 3 encompasses the area where most of the industrial shops and aircraft maintenance were located. Descriptions of the activity that occurred in these zones and the geology of these zones that follows was taken from the five-year review published in 2004 (MWH Americas, Inc. 2004).

#### 3.3.1 Zone 1

Zone 1 is located in the northeastern portion of the former base and contains several IRP sites. These include several landfills, a paint can disposal area, railroad tracks, and a bulk fuel storage area (BFSA), Site 13, where two of the monitoring wells used in this study are located. The BFSA was the main storage area for fuels at the base; it has been in operation from 1953 to the present. The BFSA encompasses approximately 16 acres and is located at the northeastern section of this zone. Currently, the BFSA contains two aboveground and two underground storage tanks, which are sur-

rounded by earthen berms. Major spills occurred at this site in 1963, 1975, and 1980.

The overburden deposits across Zone 1 include younger sediments, such as marsh deposits, and older deposits, such as glacial-marine deposits. The unconsolidated stratigraphic units identified at Pease AFB are fill, Upper Sand (US), Marine Clay and Silt (MCS), Lower Sand (LS), and glacial till. One or more of these units may be absent at any particular location. Across Zone 1, the US unit ranges in thickness from approximately 0.6 to 10 ft. The LS unit is not present in Zone 1 due to limited presence of the MCS unit. Glacial till is discontinuous across Zone 1.

The topography of the bedrock surface across Zone 1 is accentuated by several prominent highs and one prominent valley, with up to 75 ft. of relief zone-wide. A relatively large, broad bedrock high extends from the BFSA north toward Landfill 5. The bedrock consists of rocks of the Eliot Formation, which is generally composed of interbedded phyllite, metagraywacke, and quartzite.

#### 3.3.2 Zone 3

Zone 3 is located in the central portion of the former AFB and occupies approximately 440 acres. The zone contains numerous buildings with adjacent paved parking areas, a network of roads, and the flightline area. The aircraft parking apron is a major feature of the base and comprises nearly one-third of the zone. This zone contains seven IRP sites that are buildings and three underground storage tank (UST) sites. The other six wells selected for this demonstration are located at building 113 (site 32). Newfields Ditch, a storm-water drainage swale passes between Buildings 113 (Site 32) and 119 (Site 36). The ditch drains toward the northeast and eventually discharges into Hodgsons Brook.

Building 113 was used between 1955 and 1991 primarily for aircraft munitions systems and avionics maintenance (including some vapor degreasing operations). A 1,200-gallon concrete UST was located near the northeastern corner of the building and received waste TCE from degreasing operations conducted inside the building from 1956 to 1968. Sometime after 1977, use of the UST was discontinued and it was filled with sand. In 1988, the UST was excavated and removed, and an underground overflow discharge pipe associated with the UST was discovered. The soil and ground-

water contamination at this site is believed to be primarily a result of the historic use of the TCE tank and associated overflow pipe.

The shallow subsurface beneath Zone 3 generally consists of the same lithologic units found in Zone 1. The underlying bedrock is either the Kittery or Eliot formation, depending on the specific site location within Zone 3. The thickness of the overlaying, unconsolidated lithologic units varies across the site as the elevation of the bedrock interface is highly variable. Figure 4 shows a cross-section of the stratigraphy of Zone 3 on a north-south axis, and Figure 5 shows the stratigraphy on an east-west axis. These cross-sections also are characteristic of the stratigraphy of the entire site.

Regional groundwater flow is to the south-southeast within this zone under static conditions (i.e., when the Haven well is not being used). Localized flow vectors exist at each of the sites, depending upon the season. Groundwater contaminant plumes extending beyond the identified source areas have been delineated at Sites 32 and 36. The identified contaminant plumes are primarily halogenated hydrocarbons with the most extensive groundwater contaminant plume originating from Site 32.

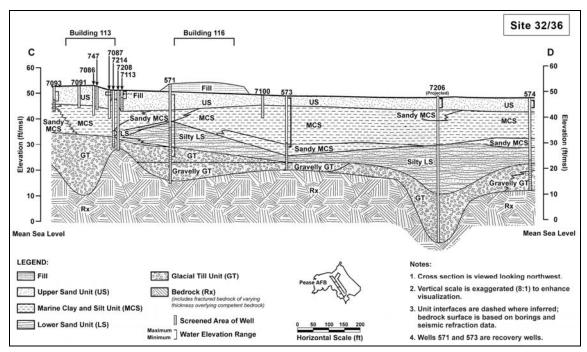


Figure 4. North-south cross section of Zone 3 (Roy F. Weston, Inc. 1992).

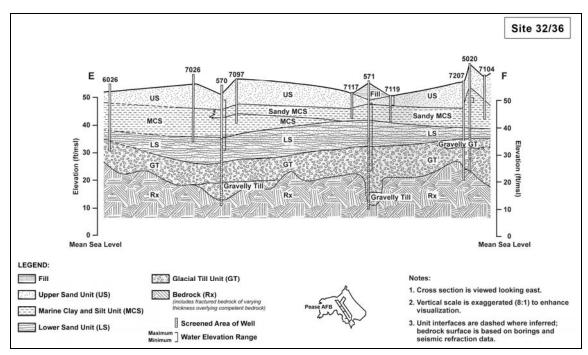


Figure 5. East-west cross section of Zone 3 (Roy F. Weston, Inc. 1992).

#### 3.4 Pre-demonstration testing and analysis

Prior to conducting a field trial for inorganic analytes, it was important to demonstrate that the Snap Sampler could also be used to collect inorganic analytes. These studies were conducted to address this question.

#### 3.4.1 First laboratory study

For this study, the procedure was similar to that described previously (Section 2.2.1). Five trigger lines of Snap Samplers, with each line containing three Snap Samplers (with 125-mL polypropylene [PP] bottles), were deployed in a standpipe. The test solution was prepared by adding Atomic Adsorption reference solutions with known volumes of As, Cd, Cr, Ni, and Zn to a 1000-mL glass beaker containing deionized (DI) water. A known weight of lead nitrate was then added to the test solution and the solution was stirred for approximately 2 hours. The concentrated test solution was added to the standpipe (already containing DI water), and the diluted test solution was then circulated for  $2\frac{1}{2}$  hours to mix it. Concentrations of As, Cd, Cr, and Pb were ~ 200 ppb in the test solution, and concentrations of Ni and Zn were ~ 400 ppb. One trigger line (with three bottles) was recovered after 24-hour, 48-hour, and 72-hour equilibrations, and additional samples were collected after 50- and 102-day equilibrations. Samples were acidified and sent to the Engineering Research and Development Center

Environmental Laboratory at Omaha, Nebraska (ERDC-EL-EP) for analyses by Inductively-Coupled Plasma (ICP), using EPA SW 846 method 6010B (U.S. EPA 1996).

Typically, As and Cr exist as anions in water while Cd, Pb, Ni, and Zn are found as cations. For the anions, we recovered 100% of the As and 98% of the Cr after 24 hours, and 100% of both analytes after 72 hours (Table 2). Recovery of the Cd cation was also 100% after 24 hours. In contrast, only 78 to 95% of the Zn, Ni, and Pb cations were recovered after the 24-hour equilibration time. After 72 hours, recovery of these analytes was essentially the same. The results for the Zn, Ni, and Pb were not surprising, given that previous studies (Masse, Maessen, and DeGeoeij 1981; Parker, Hewitt, and Jenkins 1990; Hewitt 1992; Ranney and Parker 1998b) have shown that anions are typically not sorbed by polymers such as polyethylene (PE) and polytetrafluoroethylene (PTFE), while cations are.

Analyte	Equilibration time								
Analyte	24-hr	48-hr	72-hr	50-day	102-day				
Arsenic	100.0	99.6	100.1	100.9	99.9				
Cadmium	100.7	98.0	100.5	100.7	100.6				
Chromium	98.5	98.4	99.5	100.2	113.0				
Lead	95.1	94.3	94.4	89.5	97.3				
Nickel	94.5	91.7	91.9	93.4	103.9				
Zinc	78.3	80.9	79.6	69.2	91.2				

Table 2. Percent recovery of the analytes with time.

These results suggested to us that a longer equilibration time may be needed for some of the cations. To address this possibility, one of the two remaining samplers was removed after 50 days. However, even after 50-day equilibration, there was no improvement in the recovery of these cations (Table 2).

Since 50 days should have been more than adequate time for equilibration to occur, we examined the actual concentrations of the analytes (vs. the percent recovery). If leaching had occurred, that might explain the lack of equilibration. Table 3 shows the concentrations of the various analytes with time. Concentrations of Pb, Ni, and Zn were considerably higher (1.2x - 2.3x) after 50 days than they were initially. This suggested that perhaps the metal spigot leached these analytes into the test solution as the control samples were collected. To address this possibility, we decided to collect a

control sample from inside the standpipe (bottle control) and compare it with control samples taken from the spigot (spigot control).

	Equilibration time									
Analyte	24	1-hr	48	-hr	72	-hr	50-	day	102	-day
	Control	Sample	Control	Sample	Control	Sample	Control	Sample	Control	Sample
As	195	195	195	194	194	194	188	190	187	186
Cd	209	210	210	206	207	208	204	205	204	205
Cr	196	193	196	193	194	193	192	192	198	224
Pb	197	188	198	187	199	188	231	207	231	225
Ni	373	353	387	355	398	365	478	447	478	496
Zn	438	343	428	346	441	351	1031	714	1225	1117

Table 3. Mean concentrations (µg/L) of analytes with time.

The last set of samples was collected after 102 days equilibration. To collect the bottle controls, a sample bottle was placed on a stainless steel line (with stainless steel weights), lowered quickly into the standpipe to the depth of the spigot, and allowed to fill. The following sampling order was used. First a bottle control was taken, then a spigot control, then the Snap Sampler was activated closing the sample bottles, then a second bottle control sample was collected, and finally a second spigot control was collected. The results from this trial are given in order in Table 4.

Sample	As	Cd	Cr	Pb	Ni	Zn
Bottle control 1	154	170	165	187	399	941
Spigot control 1	186	204	198	235	479	1260
Snap sample	186	205	224	225	496	1120
Bottle control 2	187	203	198	223	478	1140
Spigot control 2	187	203	198	227	476	1190
Mean bottle control	171	187	182	205	439	1040
Snap sample	186	205	224	225	496	1120
Mean spigot control	187	204	198	231	478	1220

Table 4. Analyte concentrations (µg/L) in samples collected on day 102.

Although this data is somewhat confusing (probably because the standpipe was mixed with each sampling event), it is clear that the concentration of Zn was higher in both spigot controls than it was in either the bottle control or Snap Sampler sample. These results support our hypothesis that there was leaching of these analytes (especially Zn) from the sampling spigot.

For all the data, the precision of the data (i.e., agreement between the replicate samples) was excellent, with percent relative standard deviations (%RSDs) that were less than 7.5%. However, it is interesting that for As, Cd, and Cr, the %RSDs were always less than 1.5%. In contrast, the %RSD for the leached analytes (Pb, Ni, and Zn) were generally greater for the control samples (where the %RSD ranged from 1.1 to 7.1%) than for the Snap Sampler samples (where the %RSD ranged from 0.3% to 1.8%). These findings also support the hypothesis that there was leaching from the sampling valve into the control samples.

To explore this further, we emptied the standpipe and removed the metal spigot from it. When we examined the inner surface of the spigot, we found it showed signs of significant corrosion. Thus, based on these findings and similar earlier findings from studies conducted with stainless steel well casings (Hewitt 1989; Parker, Hewitt, and Jenkins 1990; Hewitt 1992; Hewitt 1994), we concluded that the spigot served as a reservoir for leached metal constituents of Pb, Ni, and Zn, and that this sampler was able to recover representative concentrations of As, Cd, and Cr.

#### 3.4.2 Second laboratory study

For the second laboratory study, the metal spigot on the standpipe was replaced with an HDPE) spigot. The test solution was prepared by adding calcium nitrate, manganese sulfate (monohydrate), sodium chloride, potassium bromide, and magnesium perchlorate to a 5-gal glass carboy containing DI water. The carboys were filled so that there was minimal headspace and then covered with two layers of tightly fitting aluminum foil. To dissolve the analytes, the solutions were stirred for approximately one hour using a magnetic stirrer (with a Teflon-coated stir bar). After stirring the test solution, the carboy was added to the standpipe that already contained  $\sim 4$  gal of DI water. The diluted test solution was then mixed by emptying the standpipe and refilling it. Concentrations of the cations in the test solution ranged from  $\sim 8$  mg/L (for Mg) to  $\sim 42$  mg/L (for K). Concentrations of the anions in the test solution ranged from  $\sim 13$  mg/L (for nitrate) to  $\sim 80$  mg/L (for bromide).

The experimental protocol used was similar to that used in the first laboratory study, except that only three Snap Sampler trigger lines were deployed in the standpipe and each line contained only two 125-mL PE Snap Sampler bottles. One trigger line (with two bottles) was recovered after 24-hour, 48-hour, and 72-hour equilibrations. Samples were acidified and

sent to ERDC-EL-MS for analyses by Ion Chromatography, using EPA methods 300.0 (Hautman et al. 1999) and 314.0 for perchlorate (Pfaff 1993).

Tables 5 and 6 summarize our findings by showing the mean percent recovery of the cations and anions by the Snap Sampler, as compared with the control samples. For all the analytes, recovery was greater than 96% after 24 hours, and greater than 99% after 48 hours. The data for the anions and cations are summarized in Appendix Table E1 and Appendix Table E2 (respectively). These tables include the mean concentrations and the %RSD of the analytes for each sampling method, time and analyte.

Sample		(%)			
Sample	Calcium	Potassium	Magnesium	Manganese	Sodium
24-Hr	98.7	100.4	97.4	98.3	99.2
48-Hr	100.3	102.0	99.8	99.4	100.5
72-Hr	99.0	98.5	99.9	100.0	100.0

Table 5. Mean percent recovery of the cations with time.

Table 6. Mean percent recovery of th	ne anions	with time.
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Sample	Mean Recovery (%)				
	Bromide	Chloride	Nitrate	Perchlorate	Sulfate
24-Hr	99.1	96.2	100.0	100.8	101.6
48-Hr	100.6	107.0	100.8	106.1	102.4
72-Hr	98.8	100.8	99.6	110.9	100.8

#### 3.4.3 Laboratory study conclusions

Currently the ITRC Passive Sampling team recommends that most passive samplers be left in a well to equilibrate for at least two weeks (ITRC 2006, 2007). This allows the well time to recover from the disturbance caused by placing the sampler in the well and gives time for the formation to reestablish the normal flow pattern in the well. The findings from these studies demonstrate that this is more than enough time for the materials in the Snap Sampler to equilibrate with both anions and cations (including several types of metals) in the well water.

# 3.5 Testing and evaluation plan

#### 3.5.1 Demonstration installation and start-up

The eight ground water monitoring wells used in this study had an inner diameter of 10 cm (4 in.). These wells are characterized in Table 7 and their location is shown in Figure 6. Most of the wells are located near building 113 (Site 32, Zone 3), which is near an underground storage tank spill of TCE; two wells were located in a BFSA (Site 13, Zone 1). The criteria used to select these wells included well diameter, screen length, sampling depth, and detectable concentrations of the analytes of interest. The tops of the well screens varied in depth from 1.5 to 13.7 m (4 to 45 ft) below ground surface (bgs), and screen lengths varied from 1.5 to 4.6 m (5 to 15 ft). All of the screens were located below the water table.

Both before and during this demonstration, we checked with the site manager to be certain that there would not be any discontinuities in the operation of the treatment facility. This was because such discontinuities would affect ground water flow within the formation and the wells.

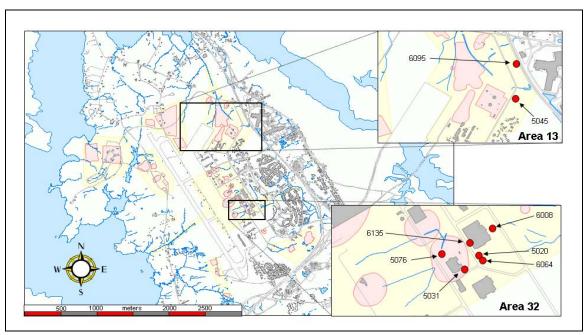


Figure 6. Map of the former base showing the locations of the monitoring wells used in this study.

								Screen	
Well #	Well Diameter (inches)	Toxics above MCLs	VOCs above MCLs?	Top of screen (ft bgs)	Bottom of screen (ft bgs)	Screen length (ft)	Approx. depth to water (ft bgs)	length in water table (ft)	
Bulk Fuel Storage Area (BFSA - Site 13)									
3-5045	4	As	yes	51	13	8	3	all	
13-6095*	4	As	no	11	21	10	6	all	
Building 11	3 (Site 32)								
32-5020	4	As	no	14.7	25.35	10.65	5	all	
32-5031	4	As	yes	13	18	5	4	all	
32-5076	4	As	no	35	45	10	5	all	
32-6008*	4	As	yes	38	52	14	3	all	
32-6064*	4	As	no	34.5	44.5	10	5	all	
32-6135*	4	As	yes	45	60	15	7	all	

Table 7. Information on the wells used at the former Pease AFB.

#### 3.5.1.1 Well development

Preliminary assessment of the wells revealed that most had large amounts of silt in them. Since it was important that the wells function properly, we redeveloped all of them prior to conducting any further field work. The wells were redeveloped using a surge-and-purge technique. However, we were not able to obtain clear water in three of the eight wells. Specifically, substantial turbidity remained in the pumped water following redevelopment in wells 32-5020 and 32-6135, and there was slight turbidity in water from well 13-6095. Two of these wells (32-6135 and 13-6095) were bedrock wells. Two of the wells (13-6095 and 32-5020) were relatively shallow wells. Well 32-6135 had the longest screen (15 ft).

#### 3.5.1.2 Flow meter testing

Once the wells were redeveloped, the hydraulics in each well were determined by using a heat pulse flow meter. These tests were conducted under both static and low-flow pumping conditions.

The heat pulse flow meter works by generating a "heat pulse" which is directly transferred to the water surrounding the element. The heated water then travels vertically along with the flow in the well, if any vertical flow is

<sup>\*</sup> bedrock well

<sup>&</sup>lt;sup>6</sup> The flow meter used was manufactured by Mount Sopris Instruments of Golden, Colorado.

present. Sensors above and below the heating element detect the arrival of the heated water, which is recorded and displayed on the field computer used to run the tests. Travel time of the heat pulse, along with borehole diameter, is used to calculate flow rate within the bore. The flow meter software reports the flow rate in gallons per minute (gpm). In the case where there is no vertical flow in the well, the heated water will slowly approach the upper sensor as a result of the buoyancy of the heated water. This artifact of upward vertical flow can be discerned from true vertical flow by comparing velocities in known locations where there is no vertical flow (e.g., in the blank casing).

Calibrations to "no vertical flow" were conducted in the blank casing in the first well. The calibration was conducted to establish a baseline for appearance of the buoyant heat pulse at the upper sensor under known noflow conditions. Repeated measurements were consistent, showing an upward "flow" of less than 0.01gpm. Arrival of the heat pulse under no-flow conditions was 70-90 sec. This instrument could not detect a flow rate lower than 0.01 gpm in these wells

## **Ambient vertical flow testing**

For the ambient flow testing, the flow meter was deployed at the middle of the screen. The tool was then left to equilibrate in the well for 10 to 30 minutes. This allowed the water level in the well to be reestablished, following insertion of the probe. Following the equilibration, several readings were collected at each well to determine consistency of the results.

Ambient (non-pumping) flow test data indicated that there was measurable vertical flow in only one of the eight wells, well 32-5031 (Table 8). However, the velocity of the flow in this well was slight, just above the detection capability of this method for this well (0.01 gallons per minute), and was in a negative direction. Thus, under normal ambient conditions (i.e., when the well was not pumped), there is a slight downward vertical flow in this well. Generally, one expects to find vertical flow in the wells with longer screens (especially those that are 20 ft or more), where there is a difference in hydraulic head. Given that the well screens in this study were all less than 20 ft in length, it is not surprising that we did not have vertical flow in most of these wells. However, it is interesting that the one well where we found slight vertical flow was actually the well with shortest screen length (5 ft).

Well	Screen*	Probe Position*	Vertical Flow
32-6064	36.2-46.2	41.3	None detected
32-5020	15.8-26.5	21.1	None detected
32-5031	14.9-19.9	17.4	-0.48 cm/min
32-5076	38.0-48.0	43.0	None detected
32-6135	46.9-61.9	54.5	None detected
32-6008	39.4-53-4	46.4	None detected
13-5045	6.3-14.3	10.3	None detected
13-6095	13.2-23.2	18.4	None detected

Table 8. Ambient (non-pumping) flow testing results

#### **Dynamic vertical flow testing**

After completion of the ambient testing in a well, dynamic (pumping) tests were conducted. The heat pulse flow meter was left at a mid-screen position during the first phase of the dynamic tests. Flow within the screen interval was induced by pumping with a peristaltic pump above the screen interval in each well (all wells had fully submerged well screens— i.e., none of the wells were water table wells). Low-flow rates were used to simulate flow rates anticipated for subsequent low-flow purging and sampling. Flow rates at the wells during the dynamic tests ranged from 170 to 430 mL/min. Steady-state (no further drawdown) conditions were established prior to collecting measurement data. Several heat pulse measurements were taken at each mid-screen deployment to determine consistency of the measurements.

Following the mid-screen measurements, the flow meter sensor was raised above the screen level. Additional measurements were conducted in the blank casing at the same pumping flow rate. These measurements allowed a calibration of each well's full flow. During steady drawdown conditions, all water being pumped must come from the well screen. Therefore, simple calculations can be made using the mid-screen flow rate and full-screen flow rate, to estimate contribution of the upper and lower portions of the well.

Results from the flow meter testing under pumped conditions are presented in Table 9. The measurements indicated a variety of flow patterns in the test wells. Some wells showed nearly equivalent contributions from the top and bottom portions (e.g., wells 32-5020 and 32-6135). Three of

<sup>\*</sup> Measurements in feet below top of casing

the four bedrock wells showed a significant contribution from one portion of the screened interval under pumped conditions. Specifically, wells 32-6008 and 32-6064 showed significant contributions from the upper zone, and wells 13-6095 and 32-5076 (not a bedrock well) showed significant contributions from the deeper portion of the well. The results for well 32-5031 were anomalous in that the flow rate for the full casing was less than the flow rate for the bottom half of the well. This well had the only detectible ambient vertical flow and also had the shortest (5-ft) screen. It is unclear what is the mechanism for the discrepancy, but the ambient vertical flow component is likely contributing to the ambiguity in this case. Some of the data for well 13-5045 was lost, which resulted in unreliable wholescreen vs. mid-screen flow rates.

Well	Date	Screen*	Probe Positions*	Flow Rate ml/min	Flow %, bottom half	Flow %, top half
32-6064	5/21/07	36.2-46.2	41.3 / 34.9	400	10	90
32-5020	5/21/07	15.8-26.5	21.1 / 15.0	400	55	45
32-5031	5/22/07	14.9-19.9	17.4 / 13.9	400		
32-5076	5/22/07	38.0-48.0	43.0 / 37.0	260	70	30
32-6135	5/22/07	46.9-61.9	54.5 / 46.0	170	45	55
32-6008	5/23/07	39.4-53-4	46.4 / 38.4	430	5	95
13-5045	5/23/07	6.3-14.3	10.3 / 5.8	400		
13-6095	5/23/07	13.2-23.2	18.4 / 12.7	400	80	20

Table 9. Active pumping flow testing results.

#### 3.5.1.3 Profiling contaminant stratification with depth in the wells

Following completion of the borehole flow meter tests, two Snap Samplers, each on its own trigger line, were deployed in each well (Figure 7). The trigger line for the bottom sampler contained a baffle that divided the well screen in half, yielding an upper and lower zone. The trigger line for the upper sampler also had a baffle that was placed 0.5 ft above the top of the well screen. This was done to separate the screen from the blank casing. Both samplers were placed in the middle of their respective zones. The decision was made not to vertically profile well 32-5031 because the screen was only 5 ft in length and so only one sampler was placed in this well. For all the wells, a baffle was placed above the sampler to separate the screen from the blank casing. The samplers were left in the well for one week prior to collecting the samples.

<sup>\*</sup> Measurements in feet below top of casing

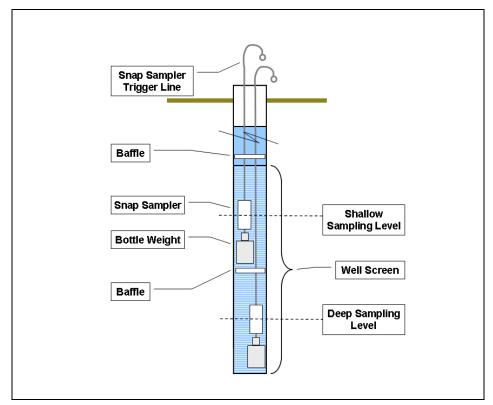


Figure 7. Diagram showing vertical profiling of well using Snap Samplers.

The baffles consisted of two circular discs of 0.030-in-thick PE, sized slightly larger than the inside diameter of the well. Around the outside of the disc, slits were cut to allow the baffles to deform slightly so that the baffle fit tightly within the well. The slits in the two discs were misaligned to limit water exchange. The discs are attached to the Snap Sampler trigger line with plastic snap-on grips ("Herbie" clamps). Figure 8 shows a photo of a trigger line with a baffle. Because of the relatively light weight of the samplers and the resistance to lowering the samplers in the well caused by the baffles, we had to add a weight to the bottom. For each string of samplers, we added a 1-liter plastic water bottle filled with sand as a bottom weight.

Once the samples were collected, they were placed on ice, acidified, and sent by overnight courier to the laboratory for analyses.

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Figure 8. Photo of Snap Sampler, trigger line, and baffle.

Table 10 shows the results from vertically profiling analyte concentrations in the wells. For most of the wells, there was no substantial difference between the analyte concentrations in the sample collected from the shallow vs. the deeper portion of the well. The most notable exception was well 32-5020, where concentrations of all the analytes (except Na) were higher in the deeper part. However, this difference was believed to be caused by the heavier sediment load found in the deeper sample (Figure 9). This is one of the wells we were not able to successfully redevelop, and we suspect that the filter pack and/or screen for this well may not have been correctly sized and thus was unable to prevent fines from entering the well. Two of the bedrock wells also showed concentration gradients with depth for As and Fe. Wells 32-6064 and 13-6095 both had slightly higher concentrations of these analytes in the shallow portion of the well.

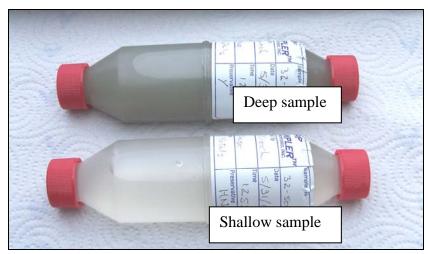


Figure 9. Sediment load comparison between two samples from well 32–5020.

Table 10. Results from the depth profiles of the wells.

Well	Donth			Concer	ntration (ı	mg/L)		
Well	Depth	As	Ca	Fe	Mg	Mn	K	Na
13-5045	shallow	0.15	67	17	11	5.4	2.5	80
13-5045	deep	0.14	61	17	12	6	2.9	110
13-6095	shallow	0.14	29	7.9	6.3	3.9	1.2	10
13-6095	deep	0.065	28	3.7	5.9	3.7	1.1	11
	_							
32-5020	shallow	0.15	190	9.8	44	0.53	8.4	60
32-5020	deep	0.25	230	160	82	2.9	33	60
	_							
32-5031	single depth	0.11	89	12	21	0.4	5.2	30
32-5076	shallow	0.093	65	7.4	14	0.39	4.6	30
32-5076	deep	0.089	52	8.8	14	0.36	4.9	30
	<b>,</b>	1				1		
32-6008	shallow	0.066	65	1.5	24	0.15	7.3	70
32-6008	deep	0.057	69	1.2	24	0.15	7.2	70
32-6008	deep dupl.	0.060	65	1.3	24	0.15	7.2	80
	<b>,</b>	1				1		
32-6064	shallow	0.11	150	2.6	42	0.27	9.2	50
32-6064	deep	0.030	140	0.2	40	0.34	9.0	60
	1		T		1		1	
32-6135	shallow	0.022	3.7	2.1	1.6	0.038	6.2	120
32-6135	deep	0.021	4.5	2.9	1.6	0.059	6.4	130

## 3.5.1.4 Equipment blanks

A small diameter (¾ in.) bladder pump (the Mini Bladder Pump<sup>7</sup>) was installed in each of the wells used in the field study. However, prior to deploying these pumps in the wells, equipment blanks were drawn. This testing was conducted in our laboratory. The pumps were placed in a 94-cmtall x 16.5-cm-dia (37 in. x 6.5 in.) pipette washer containing house distilled water. All the pumps were connected to the pump controller at the same time via a manifold of Teflon tubing and left pumping overnight. During this time, the pumps were pressurized for 1 sec and exhausted for 1 sec at a gauge pressure of approximately 6–8 psi. Pumped water was drained into the sink while the pipette cleaner was continuously replenished with house distilled water. After 22 hours of pumping, the water supply was switched to the DI water system, and they were left to pump at the same rate for another 1.5 hours. The pumps were then shut off for  $\sim 4$ hours, after which the pipette cleaner was emptied and refilled with fresh DI water. After another 45 minutes of pumping continuously-replenished DI water, sample blanks were pumped through 6.35 mm-diameter Teflonlined polyethylene tubing (each ~ 0.75 m in length) into 125-mL, HDPE bottles containing nitric acid as a preservative. After the pumps were removed from the pipette cleaner, two samples of the water in the pipette cleaner were drawn off through the bottom stopcock. The water in the pipette washer was then drained and refilled with fresh DI water and a trigger line with two Snap Samplers (with 125-mL PP bottles) was placed in the pipette washer. After 10 minutes, the samplers were triggered, recovered, and acidified with 0.5 mL of nitric acid. All samples were stored in a refrigerator at 4°C overnight, packed on ice the next morning, and were transported to the contract lab for analysis (~ 1 hour away). The samples were analyzed for total metals. (A description of the handling and analyses of the samples is given in detail in Section 3.5.7.2.)

Additional blank equipment samples for the Snap Samplers and the RGC samplers were collected as follows. Two trigger lines, each with one Snap Sampler (125-mL PP bottle) were deployed in the pipette cleaner filled with DI water. At the same time, one RGC sampler was deployed in a widemouthed 5-L HDPE bottle filled with DI water. After leaving the samplers for two weeks, the Snap Samplers were triggered and the RGC sampler was removed from its container. The RGC sample was transferred to a 125-mL PE bottle with nitric acid preservative. The Snap Samplers were re-

<sup>7</sup> The pump used is manufactured by Durham-Geo Slope Indicator (DGSI) of Stone Mountain, GA.

2291

2116

2270

1400

moved from the pipette washer one at a time. The first sample was not acidified. The second sample was preserved with nitric acid. Two samples of water were then drawn directly from the pipette cleaner through the stop cock at the bottom of the washer into (125-mL) PE bottles, containing nitric acid as a preservative. These samples were stored in a refrigerator (at  $4^{\circ}$ C) for the weekend. The following Monday morning, the samples were placed on ice in a cooler, and they were then picked up by a courier and delivered to the laboratory. The unacidified samples were analyzed for dissolved metals and the acidified samples were analyzed for total metals. (Again, a description of the handling and analyses of the samples is given in detail in Section 3.5.7.2.)

Generally, concentrations for the blank samples indicated that leaching of constituents from the test equipment was not a concern. For the Snap Sampler, concentrations in the equipment blanks were at or below the detection limit for the unfiltered samples. Concentrations of most of the analytes in the RGC blanks were also at or near the detection limit, with the exception of Ca for which the concentration was very slightly elevated. The results for the pumps indicated that there were no issues with analytes leaching from the pumps (Table 11). For all analytes except for Fe, concentrations were either at or below the detection limit. Concentrations of Fe were also generally below the detection limit, with a few exceptions. The concentration of Fe in the water from the pipette washer was equivalent to that found in a few of the pumps and in the filtered Snap Sampler sample. This indicates that the pumps and Snap Sampler were not the source of the elevated iron.

Concentration mg/L Pump No. As Ca Fe Mn Κ Na Mg 1470 < 0.001 < 0.05 < 0.05 < 0.05 < 0.005 < 0.05 <5 2269 <0.001 < 0.05 < 0.05 < 0.05 < 0.005 < 0.05 <5 2272 <0.001 < 0.05 < 0.05 < 0.05 < 0.005 < 0.05 <5 1472 <0.001 < 0.05 < 0.05 < 0.05 < 0.005 < 0.05 <5 2292 <0.001 < 0.05 0.07 < 0.05 0.006 < 0.05 <5 2271 <0.001 < 0.05 0.20 < 0.05 < 0.005 < 0.05 <5

< 0.05

< 0.05

0.15

0.08

< 0.05

< 0.05

<0.05

< 0.05

< 0.005

< 0.005

<0.005

< 0.005

< 0.05

< 0.05

< 0.05

< 0.05

<5

<5

<5

<5

< 0.05

< 0.05

< 0.05

< 0.05

< 0.001

< 0.001

<0.001

<0.001

Table 11. Results for the equipment blanks.

Other equipment			Conce	ntration i	ng/L							
Other equipment	As	Ca	Fe	Mg	Mn	K	Na					
Pipette bucket	<0.001	<0.05	0.19	<0.05	<0.005	<0.05	<5					
Snap Sampler	<0.001	<0.05	<0.05	<0.05	<0.005	<0.05	<5					
Dup. Snap Sampler	<0.001	<0.05	<0.05	<0.05	<0.005	<0.05	<5					
RGC (unfiltered)	<0.001	0.13	<0.05	<0.05	<0.005	0.07	<5					
Snap (unfiltered)	<0.001	<0.05	<0.05	<0.05	<0.005	<0.05	<5					
Snap (filtered)	<0.001	<0.05	0.05	<0.05	<0.005	<0.05	<5					
Pump (unfiltered)	<0.001	<0.05	<0.05	<0.05	<0.005	<0.05	<5					
Pump (unfiltered) Lab Duplicate	<0.001	<0.05	<0.05	<0.05	<0.005	<0.05	<5					
Pump (filtered)	<0.001	<0.05	0.19	<0.05	<0.005	<0.05	<5					
Lab Filter Blank	<0.001	<0.05	<0.05	<0.05	<0.005	<0.05	<5					

#### 3.5.1.5 Initial low-flow sampling of the wells

After the bladder pumps were deployed in the wells, preliminary unfiltered low-flow samples were collected from all the wells. This was done for four reasons: (1) to determine the initial analyte concentrations, (2) to confirm the flow rate to be used would not cause excessive drawdown in the wells, (3) to determine the sampling time for low-flow sampling (needed for the cost analyses), and (4) to equilibrate materials in the pump and tubing with analytes in the well water (to reduce possible losses due to sorption that might occur).

The samples were collected using the EPA's low-flow purging and sampling protocol (U.S. EPA Region 1 1996). The purge parameters were monitored using a Horiba (MDL W-22XD) probe and a flow-through cell. Purge parameters included turbidity, DO, conductivity, salinity, pH, total dissolved solids (TDS), redox potential (ORP), and temperature. Whenever possible, turbidity was monitored until the readings were 10 nephelometric turbidity units (NTU) or less. The other parameters were monitored until three successive readings varied by no more than  $\pm$  10%. The Horiba probe was calibrated each morning using the Horiba calibration solution. This solution is used to calibrate the meter for pH, conductivity, turbidity, and DO. (The other purge parameters are calculated based on these measurements.) Equipment used to monitor purge parameters was checked approximately one month before we began the project and, again, just before beginning the field work.

The samples were collected in 125-mL acid-cleaned HDPE bottles containing diluted nitric acid (as described previously). After the sample bottles were filled, they were placed on ice in a cooler, and then shipped to the contract laboratory for analyses.

Table 12 gives the results of the initial low-flow sampling. In all cases, concentrations of the analytes of interest were well above the detection limit and well above any blank values that could have interfered with data analyses.

Well No.			Conce	entratio	on mg/L							
Well No.	As	Ca	Fe	Mg	Mn	K	Na					
32-6064	0.072	160	1.1	47	0.36	9.0	60					
32-5020	0.15	210	3.4	50	0.56	6.6	60					
32-5031	0.088	51	5.2	16	0.37	3.8	50					
32-5076	0.058	46	1.6	11	0.42	3.4	30					
32-6135	0.022	3.1	0.42	1.3	0.032	5.8	130					
13-5045	0.15	42	11	9.3	6.5	2.0	100					
32-6008	0.060	89	0.60	32	0.23	7.4	80					
13-6095	0.055	25	3.0	5.6	5.9	1.1	10					
13-6095 (Dup.)	0.058	29	3.3	6.4	5.6	1.2	10					

Table 12. Results from initial low-flow sampling of the wells.

## 3.5.1.6 Unanswered questions concerning long-term use of Snap Sampler

One unanswered question with respect to using passive sampling methods is whether the wells that are sampled using this technology will require more frequent re-development than with low-flow sampling.

# 3.5.2 Period of operation

Task	Start Date	Finish date
Preliminary site visit	13-Mar-07	13-Mar-07
Well development	23-Apr-07	2-May-07
Flowmeter testing	21-May-07	23-May-07
Profile contamination in wells	24-May-07	31-May-07
Equipment blanks - pumps	29-May-07	30-May-07
Preliminary Low-Flow sampling	5-Jun-07	7-Jun-07

Table 13. Dates for the various demonstration activities.

Task	Start Date	Finish date
Deploy samplers for round 1 (8 wells)	4-Jun-07	7-Jun 07
Round 1 sampling	18-Jun-07	29-Jun-07
Equipment blanks - Snap & RGC samplers	15-Jun-07	18-Jun-07
Deploy samplers for round 2 (2 wells)	6-July 07	6-July 07
Round 2 sampling	23-Jul-07	23-Jul-07

## 3.5.3 Amount / treatment rate of material to be treated

Not applicable.

#### 3.5.4 Residuals handling

The only wastes that were generated were the purge water and the spent disposable water from the RGC samplers. After transferring an aliquot from each of the RGC samplers, they were placed in a plastic garbage bag and disposed of as directed by the site manager. The purge water was containerized and taken to the onsite treatment plant for disposal.

## 3.5.5 Operating parameters for the technology

An equilibration time is required for all diffusion passive samplers and is recommended for all equilibrated-grab passive samplers. Thus, the Snap Samplers and the RGC samplers needed to be deployed prior to the sampling day. The RGC samplers typically require an equilibration time of  $\sim$ 7 days for metals. While the Snap Sampler does not require as long an equilibration time for most analytes as do other diffusion samplers, the Snap Samplers were deployed at the same time so that the lines could be tethered (to reduce tangling of the lines). To allow for adequate equilibration for both types of passive samplers, the samplers were left in the well for at least 10 days prior to sample collection.

For this study, two trips to the field were required, one to deploy the samplers and one to retrieve them. However, for routine monitoring, the second trip to the field could be eliminated for the Snap Sampler. This could be accomplished by placing new bottles in the Snap Sampler after removing the sample bottles from the sampler and then placing the sampler (with the new bottles) back into the well and leaving them until the next sampling event. However, it is not possible to eliminate a second trip to

the field for the RGC samplers because they are subject to biodegradation and cannot be left in the wells for quarterly (or longer) sampling events.

Labor requirements for the Snap Samplers included: (a) moving the equipment needed for sampling to the site (relatively little needed), (b) assembling the samplers and placing them in the wells, (c) measuring the depth to water and decontaminating the water-level probe after removing it from the well, (d) retrieving the samplers from the well, (e) removing the bottle from the sampler, (f) adding preservative, (g) labeling the samples, (h) placing the samples on ice and preparing them for shipment to the laboratory, and (i) site clean-up.

Labor requirements for the RGC Samplers included: (a) constructing the samplers (prior to going to the field), (b) moving the equipment needed for sampling to the site (relatively little needed), (c) placing the samplers in the well, (d) measuring the depth to water and decontaminating the water-level probe after removing it from the well, (e) retrieving the samplers, (f) transferring aliquots of sample to sample bottles (already containing preservative), (g) labeling the samples, (h) placing them on ice and preparing them for shipment to the laboratory, (i) disposing of the spent sampler wastes (minimal volume), and (j) site clean-up.

Labor requirements for low-flow sampling included: (a) cleaning the bladder pumps (a one-time event), (b) placing the pumps in the wells (a one-time event), (c) checking the equipment (used to monitor the purge parameters) prior to going into the field, (d) calibrating the purge-parameter equipment, (e) moving a considerable amount of equipment to the site (including a generator and air compressor), (f) measuring the depth to water and the purge parameters until stabilization occurred, (g) collecting the samples in sample bottles (containing the acid preservative), (h) labeling the samples and placing them on ice, (i) preparing the samples for shipment to the laboratory, (j) disposing of the purge water, (k) decontaminating the purge-parameter equipment, and (l) site clean-up.

Because many types of samples were collected at the same time, two individuals were needed for the field study. However, only one individual would be needed to conduct the sampling using either of the passive methods. While the same is true for low-flow sampling, typically most contractors would send a field crew of two to conduct this kind of sampling. Note that if only one person conducted the low-flow sampling, it would

definitely take longer (than using a crew of two) because of the effort involved in setting up and tearing down equipment at the site.

## 3.5.6 Experimental design

The objectives for this demonstration/validation project were to demonstrate that the Snap Sampler passive ground water sampling technology can provide (1) technically defensible analytical data for the wide spectrum of analytes that are of concern to the DoD and (2) substantial cost savings. The initial experimental plan included collecting samples at five sites for a range of analyte types including VOCs, explosives, perchlorate, metals, and natural attenuation parameters. At each site, samples were to be collected with (1) the Snap Sampler, (2) low-flow purging and sampling (EPA Region 1, 1996), and (3) passive diffusion samplers such as the RGC or PDB samplers. Using these three sampling technologies allowed us to compare dissolved and colloid-borne contaminants (such as metals and the more hydrophobic organic contaminants). The site selected for this demonstration was the former Pease AFB where the analytes of interest were inorganic analytes, including several types of metals including the Alkali metals (Ca, Mg), alkaline earth metals (Na, K), and transition metals (Mn, Fe).

The initial hypothesis tested was that there were no statistically significant differences between the analyte concentrations in samples taken with the three sampling methods. That is, concentrations of the analytes in samples taken with the Snap Sampler were similar to those taken using low-flow sampling, and those taken using the Snap Sampler were similar to those taken using the RGC sampler, and those taken using the RGC sampler were similar to those taken using the low-flow sampling. However, when comparing these sampling methods, it is important to remember that currently there is *no* sampling method that yields the true analyte concentrations in the formation. Each of these sampling methods attempts to determine the analyte concentrations differently. The findings from this demonstration will be used to better define the appropriate use of each passive method.

#### 3.5.7 Sampling plan

There were 10 sampling events in this demonstration. A sampling event consisted of collecting samples from the same well using the Snap Sampler, low-flow purging and sampling (U.S. EPA Region 1 1996), and the RGC sampler. There were eight wells on the test site that met our require-

ments for this study. Therefore, all were sampled during the first round of sampling, and two of these wells were sampled a second time (i.e., for the second sampling round). Analytes of interest included As, Ca, Fe, Mg, Mn, K, and Na.

Two sets of Snap Sampler and low-flow samples were collected from each well: (1) whole-water samples and (2) samples that were filtered in the laboratory. Only one RGC sampler was collected from each well as those samples are already pre-filtered by the RGC membrane, which has a pore size of 18 Å. The intent of having both filtered and unfiltered samples was to allow comparison of colloidal-borne and dissolved metal species. Additional quality assurance (QA) / quality control (QC) samples were also collected and will be discussed later.

Two 125-mL PP Snap Sampler bottles were deployed in each well. The RGC Samplers that were deployed in the Pease wells were constructed the morning before departure for the field site. After construction, they were placed in 1-gal plastic, zip-closure bags filled with distilled, de-ionized water, and placed in a cooler with ice for transport to the field. Early the next morning, four samplers were placed in a wide-mouth, 5-L HDPE screwcap bottle that was filled with DI water so that the samplers were fully immersed. Nitrogen gas was then fed under low pressure via tubing to the bottom of the container, and the samplers were sparged for at least 90 minutes. Once work was complete at that site, the tank was disconnected and a replacement RGC sampler was added to the bottle. The sparging process was then repeated at the next site. The samplers were not sparged overnight, but the same process was followed each morning. For the second round of sampling, four RGC samples were sparged for two hours in the lab before taking them to the field. The samplers were then sparged for at least another hour prior to deployment in the well.

The Snap and RGC samplers were deployed at the same depth in the well as the intake of the bladder pump used to collect the low-flow sampling. A small-diameter (3/4-in.) pump was used in these studies so that all the equipment could be placed in the well at the same depth at the same time. The pump was placed at approximately the midpoint of the well screen. The baffle was positioned 0.5 ft above the top of the well screen. The two Snap Samplers were deployed in tandem on the same trigger line, one just above the pump intake and one just below the pump intake (Figure 10). In the first round of sampling, the RGC samplers were attached to the side of

the pump (so they didn't cover the pump inlet) and the Snap samplers were deployed separately. In the second round of sampling, the three pieces of sampling equipment were bundled together (again making certain that the pump inlet was not covered with other equipment). Again, a 1-liter plastic water bottle filled with sand was added to the string of samplers and was used as a weight to facilitate deployment of the equipment and the baffle in the well. The samplers were left to equilibrate in the well for at least two weeks prior to sampling the wells.

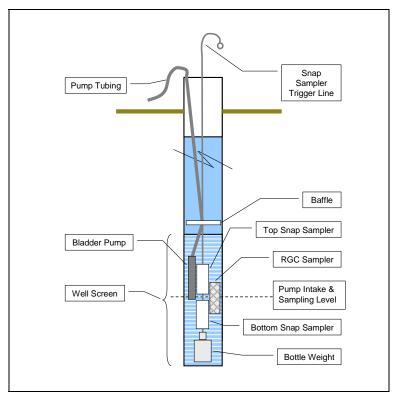


Figure 10. Diagram of deployment of sampling equipment in each well.

#### 3.5.7.1 Sample collection

The dates of the sampling events were given previously in Table 13. The low-flow samples were collected using the EPA's low-flow purging and sampling protocol (U.S. EPA Region 1 1996). The purge parameters were monitored as described previously in section 3.5.1.5. It typically took between 30 and 90 minutes for the purge parameters to stabilize, although some wells took considerably longer to stabilize.

The following sampling order (as outlined in the Demonstration Plan) was developed to reduce the influence of the various samplers on each other, and to minimize the impact of sampling on sample quality (integrity). The

Snap Sampler was to be triggered first. Then the low-flow samples would be collected as described by the U.S. EPA Region 1 (1996). Once the low-flow samples were collected, the RGC Sampler would be removed from the well and an aliquot transferred to a sample bottle. Finally, the Snap Sampler would be removed from the well and the sample bottles removed from the Snap Sampler. The flow rate, the purge parameter readings, and the time for all the events during sampling were recorded in a bound green field notebook. Because prolonged exposure to air can allow oxygen to diffuse through the RGC membrane thereby impacting some metal concentrations that are subject to oxidation/precipitation reactions and because the Snap Sampler samples remain sealed under *in-situ* conditions during this time, the RGC sample was transferred to a sample bottle prior to handling the Snap Sampler samples.

However, because of concerns by one of our reviewers about the possible impact the bladder pump might have on the RGC Sampler (i.e., that it might draw water into the sampler) we decided to collect the RGC samples prior to collecting the low-flow samples. So, for the first two wells sampled, the following sample order was used. The Snap Sampler was triggered first. Then the pump and RGC sampler were removed from the well (they were bundled together) and an aliquot from the RGC sampler was transferred to a sample bottle. Next, the Snap Sampler was removed from the well, and the sample bottles were removed from the Snap Sampler. Once these samples were processed, the pump was returned to the well and the well was allowed to settle for at least 30 minutes before purging the well. The well was then purged according to the EPA's low-flow sampling protocol at a flow rate that was determined during our preliminary sampling event. Subsequently, the depth to water was monitored during low-flow sampling to insure that excessive drawdown did not occur. Purging continued until the purge parameters stabilized. Parameters that were monitored included water level, turbidity, temperature, dissolved oxygen, redox potential, and specific conductance. After the purge parameters stabilized, the low-flow samples were collected.

As we had initially suspected, we found that this protocol disturbed the wells and it took several hours for the turbidity readings in these wells to drop to the desired range (i.e., < 10 NTU). Since these wells were being sampled for several types of metals (and metal concentrations in the unfiltered samples would be affected by turbidity), we decided to conduct all the subsequent sampling events using the originally planned sampling or-

der. For the second sampling round, the first two wells were again sampled and this time, the originally developed sampling order was used. By sampling these two wells using two different sampling orders, we could compare the effect of sampling order on the analyte concentrations in the RGC samples in two wells. Because passive diffusion samplers rely on diffusion (which takes days for equilibration to occur), the time it takes to collect the low-flow samples presumably should not significantly impact analyte concentrations in these samplers.

Sample collection for the RGC sampler involved piercing the membrane with a Pasteur pipet and transferring an aliquot to an acid-cleaned 125-mL HDPE bottle containing 1:1 nitric acid as a preservative. The bottle was then capped, labeled, and placed on ice. For the Snap Sampler samples, the Snap Sampler bottles were removed from the Snap Sampler body and the bottom caps were placed on both bottles. Next, the upper bottle was capped on the top and the lower bottle was acidified and then capped. Both samples were then labeled and placed on ice. For the two low-flow samples, the whole water sample was collected in an acid-cleaned, 125-mL HDPE bottle containing acid, and the sample to be filtered in the lab was collected in a similar bottle containing no preservative.

Waterproof sample container labels and permanent markers were used to label the samples. All samples were marked with the sampling date, sampling individual, whether they were filtered, and given a sample number that will identify the site, well, and sampling method to the sampling personnel but not the laboratory. All sample numbers were recorded in a bound green field notebook. All samples were placed on ice in a cooler and kept cold until we delivered them to the laboratory for analyses. When the samples were ready to be shipped, they were placed on fresh ice, the chain-of custody forms were filled out, and the coolers were sealed prior to shipment.

Initially the demonstration plan specified that Louise Parker and Nathan Mulherin (ERDC-CRREL) would conduct the sampling at this site. However, because of Ms. Parker's health issues, Gordon Gooch (ERDC-CRREL) assisted Mr. Mulherin in the sampling, and Ms. Parker was present to supervise most of the sampling events.

## 3.5.7.2 Sample analysis.

The samples were transported by automobile to Eastern Analytical Inc. in Concord, NH (approximately one hour away) for analyses. Eastern Analytical is an EPA-certified National Environmental Laboratory Accreditation Conference (NELAC) facility. Upon arrival at the laboratory, any samples that were to be filtered were filtered with a  $0.45\mu$  Chromafil® Polyamide (Nylon) filter into a 2-oz HDPE container containing 200  $\mu L$  of a 1:1 trace-metals grade Nitric Acid/DI water solution.

For the unfiltered samples, the samples were digested prior to analyses. This was accomplished by adding 1 mL of trace-metals grade, concentrated nitric acid to 50 mL of the test solution and then digesting the sample on a bloc heater at 85°C until the volume was reduced by half. The sample was then cooled to room temperature and brought back to a 50-mL volume by adding reagent-grade water.

Analyses were conducted using Inductively Coupled Plasma /Mass Spectrometry (ICP/MS) using EPA method 200.8 (Creed et al. 1994) according to EPA SW 846 method 6020B (U.S. EPA, 1996). All samples were analyzed within the specified holding times.

For the statistical analyses, the concentration data were analyzed on an analyte-by-analyte basis. Analytes with measurable concentrations that allowed statistical analyses included As, Ca, Fe, Mg, Mn, K, and Na. In the few instances where analyte concentrations were below the detection limit, half the detection limit was used in the statistical analyses. The filtered and unfiltered data sets were treated separately. Specifically, analyte concentrations in the filtered Snap Sampler samples, the filtered low-flow samples, and the RGC samplers were compared. Concentrations in the unfiltered Snap Sampler samples, the unfiltered low-flow samples, and the RGC samples were also compared.

Standard statistical analyses were used to analyze the data. The data sets were first analyzed to determine if the data were normally distributed and if the variances were homogenous. Whenever possible, conventional parametric analyses were used. In instances where conventional parametric tests can not be used, non-parametric (ranked) tests were used. Specifically, for normally distributed data, Repeated Measures Analysis of Variance (RM-ANOVA) was used to determine if there were significant differences between the analyte concentrations in the samples collected with

different sampling methods. Differences between the treatment methods were determined using the Holm-Sidak method for pair-wise multiple comparisons. In cases where non-parametric tests had to be used, the Friedman RM-ANOVA on Ranks test was used to determine if there is a significant difference between the treatments. In the instances where a significant difference was found, the Tukey test was used to determine which treatments differed from each other.

#### 3.5.7.3 Experimental controls

In order for the statistical analyses to be as robust as possible, it is important to minimize any extraneous factors that could influence the data quality. These factors could include the following.

- Improperly functioning wells, i.e., wells that were never adequately developed or wells needing redevelopment
- Flow patterns within the wells, e.g., vertical flow within the well
- · Contaminant gradients in the well
- Differences in sampling depth of samplers
- Flow induced changes caused by a sampler
- Contaminant concentrations that are too low to measure

To address these concerns, we included the following provisions in the design of this demonstration in an effort to either quantify their impact or reduce it.

- All the wells were sampled prior to the demonstration to determine that analyte concentrations were within the desired range, that there is adequate flow in the well, and whether the wells needed redevelopment based on turbidity readings.
- All the wells were redeveloped because they contained high levels sediment.
- The flow patterns in each of the wells were determined.
- Samples were collected at two depths in the wells (using a baffles) to determine if there was contaminant stratification in the wells.
- The sampling depth for each passive sampler was matched with that of the pump intake (used for low-flow sampling).
- We developed a sampling order that reduced sampler impacts on subsequent sampling events.

#### 3.5.7.4 Data quality parameters.

To insure data validity, standard laboratory practices for analyses included the following:

- receiving, log-in, and storage of field samples
- chain-of-custody documentation
- standards preparation and analysis
- instrument calibration
- instrumentation QC
- duplicate field samples
- matrix spike samples
- · field and laboratory blanks

Prior to deploying any of the samplers or pumps, equipment blanks were collected. The latter process was described previously in more detail, in section 3.5.1.4.

Standard QC samples included duplicates and duplicates for (laboratory) spiked recoveries to determine matrix affects, and trip blanks. A minimum of 5% of the samples were analyzed in duplicate to give a measure of the precision of the laboratory and analytical method. Certified reference samples were used by the laboratory to ensure proper calibration and thus accuracy of the analyses. One out of 40 samples was a certified reference sample (2.5%). One out of 20 samples was a calibration standard (5%). For each round of sampling, there was also was filter blank sample that was analyzed for contamination of dissolved metals samples.

At least one duplicate field sample was collected each sampling day. During the course of the field sampling, duplicate samples were collected for all three sampling methods (low-flow, Snap, and RGC). The results from these analyses provide a measure of the precision (repeatability) of the field sampling methods.

Duplicate samples for spiked recoveries were collected for 5% (or 1 of 20) of the total number of samples for the purposes of preparing Matrix Spikes (MS) and Matrix Spike Duplicates (MSD). They were identified with the suffixes MS and MSD on the Chain-of-Custody Forms. These samples were used to identify matrix effects on spiked analytes of known quantity and the laboratory's precision in recognizing matrix effects.

#### 3.5.7.5 Data quality indicators

Laboratory blanks were prepared by the contract laboratory using analytefree reagent water. One laboratory blank was performed for every 20 samples (i.e., 5% of the samples). In all cases, analyte concentrations of the primary analytes (As, Ca, Fe, Mg, Mn, K, and Na) in these samples were below the detection limit.

The relative percent difference (RPD) was used to determine the degree of agreement between the sampling methods (for the analyte concentrations). The RPD was calculated for each well and analyte according to the following formula:

RPD = [[ | Conc. Sampler A - Conc. Sampler B| ] / [Mean Conc. Sampler A & B] ] · 100

The number of wells where the RPD was 25% or less for concentrations at or above 50  $\mu$ g/L (or 50% for concentrations less than 50  $\mu$ g/L) was determined, and the percent agreement between the two sampling methods was determined from the total number of wells.

The agreement between the field duplicate samples and the original samples was excellent with RPDs 15% or less for all the samples, and in all but four instances the RPD was less than 10% (Table 14). This is well below our guideline of a 25% RPD.

Table 14. Results for field duplicate samples, with relative percent difference calculations.

	_		Cor	centration (	mg/L)		
Sample type	As	Ca	Fe	Mg	Mn	K	Na
low flow	0.095	170	1.8	52	0.37	11	71
low flow	0.10	180	2.1	52	0.40	12	73
RPD (%)	5.1	5.7	15	0.0	7.8	8.7	2.8
		•					
low flow	0.054	58	2.3	13	0.52	3.8	26
low flow	0.052	62.	2.1	13	0.54	4.0	27
RPD (%)	3.8	6.7	9.1	0.0	3.8	5.1	3.8
		•					
low flow	0.16	72	15	12	7.3	2.8	140
low flow	0.16	70	15	12	7.8	2.7	160
RPD (%)	0.0	2.8	0.0	0.0	6.6	3.6	13
	•	•	•	•	•	•	•
low flow	0.093	110	1.8	38	0.20	9.0	53
low flow	0.088	110	1.8	38	0.21	9.4	56
RPD (%)	5.5	0.0	0.0	0.0	4.9	4.3	5.5

Sample type			Conce	ntration (mg	/L)		
	As	Ca	Fe	Mg	Mn	K	Na
low flow	0.055	25	3.0	5.6	5.9	1.1	10
low flow	0.058	29	3.3	6.4	5.6	1.2	10
RPD (%)	5.3	15	9.5	13	5.2	8.7	0.0

Five percent of the samples were analyzed in duplicate to give a measure of the precision of the analyses (laboratory duplicates). The agreement between the concentrations of the analytes in these samples was also good. The RPD was less than 10% in all but three instances, was less than 15% in all but one instance, and was less than the guideline of 25% in all cases (Table 15).

Table 15. Results from duplicate laboratory analyses, with relative percent difference calculations.

Cananda tura			Co	ncentration	(mg/L)						
Sample type	As	Ca	Fe	Mg	Mn	K	Na				
Snap	0.054	42.0	2.40	8.0	7.80	1.60	14				
Snap	0.052	41.0	2.40	7.5	7.60	1.50	14				
RPD (%)	3.7	2.4	0.0	6.3	2.6	6.3	0.0				
low flow	0.056	42.0	3.30	7.6	6.40	1.50	14				
low flow	0.058	44.0	3.30	7.8	7.90	1.50	14				
RPD (%)	-3.5	-4.7	0.0	-2.6	-21	0.0	0.0				
low flow	0.059	98.0	0.62	34.0	0.220	10.0	95				
low flow	0.057	93.0	0.60	33.0	0.200	9.7	90				
RPD (%)	3.4	5.2	3.3	3.0	9.5	3.0	5.4				
Snap	0.054	42.0	2.40	8.0	7.80	1.60	14				
Snap	0.052	41.0	2.40	7.5	7.60	1.50	14				
RPD (%)	3.8	2.4	0.0	6.5	2.6	6.5	0.0				
low flow	0.068	140	<0.05	38.0	0.430	7.10	57				
low flow	0.068	150	<0.05	43.0	0.450	7.50	66				
RPD (%)	0.0	-6.9	0.0	-12	-4.5	-5.5	-15				
	_										
low flow	0.093	110	1.80	38.0	0.200	9.00	53				
low flow	0.087	110	1.70	41.0	0.200	8.60	55				
RPD (%)e	6.7	0.0	5.7	-7.6	0.0	4.5	-3.7				

For the Matrix Spike and Matrix Spike Duplicate samples, there generally was close agreement between the duplicates (Table 16). Recovery of the spiked analytes was  $100\% \pm 10\%$  for Ca, Fe, Mn, K, and Na and recovery of As was only slightly higher at 112%.

Table 16. Data for matrix spike and matrix spike duplicate samples.

Sample			Percer	nt Recovery o	f Spike		
Sample	As	Ca	Fe	Mg	Mn	K	Na
MS	104	108	97	108	82	101	106
MSD	106	103	102	104	84	100	107
MS	110	111	96	99	95	91	117
MSD	100	101	93	96	88	90	111
MS	111	99	103	95	93	91	95
MSD	111	93	98	90	87	93	99
MS	121	127	99	110	97	107	111
MSD	115	123	100	104	94	106	109
MS	115	126	94	119	101	122	123
MSD	113	130	94	119	101	115	113
MS	119	85	105	120	101	118	124
MSD	119	96	103	121	103	116	123
MS	110	96	98	92	102	96	95
MSD	108	96	97	95	104	96	96
Mean	112	107	99	105	95	103	109
Standard Deviation	5.98	14.5	3.72	11.2	7.41	11.1	10.3
Mean RSD %	5.4	13.6	3.8	10.6	7.8	10.7	9.4

3.5.7.6 Calibration procedures, quality control checks, and corrective action

All laboratory data was reviewed for completeness, detection and quantitation limits, QA/QC analyses, and the adequacy of the holding times.

The analytical laboratory used standard EPA protocols for calibrating the analytical instrumentation, including calibration curves for at least three standards at different concentrations, internal and external standards, and testing blanks. Any issues were to be reported to the PI immediately, but there were none. Certified reference samples were used by the laboratory to ensure proper calibration and accuracy of the analyses. In all cases, the certified reference samples were within 10% of the known values, well within the 20% guideline (Table 17).

Percent Recovery						
As	Ca	Fe	Mg	Mn	К	Na
101	109	95	104	90	94	105
104	109	101	98	91	102	95
102	100	108	95	100	106	96
107	103	110	108	109	102	110
106	103	99	105	99	108	105
107	103	110	108	109	102	110
110	104	109	104	104	105	106

Table 17. Percent recovery of reference samples.

#### 3.5.8 Demobilization

After sampling was complete, the RGC samplers were placed in garbage bags and disposed as trash (per guidelines of the site manager). The Snap Sampler was packaged in zip-locking plastic bags and returned to our laboratory (CRREL) for decontamination. The bladder pumps were removed from the sampling tubing, bagged, and returned to CRREL for decontamination. The sampling tubing (for the bladder pump), sampling lines (for the RGC samplers) and trigger lines (for the Snap Sampler) were placed in garbage bags and disposed of as trash (per instructions from the site manager).

# 3.6 Selection of analytical/testing methods

Analyses were conducted using standard EPA methods: i.e., Inductively Coupled Plasma /Mass Spectrometry (ICP/MS) using EPA method 200.8 (Creed et al. 1994) according to EPA SW 846 method 6020B (U.S. EPA, 1996).

# 3.7 Selection of analytical/testing laboratory

Our primary criteria for a laboratory were that it be (1) able to conduct the required analyses within the time frame needed, (2) an EPA NELAC-certified laboratory (NH certificate number 101208), and (3) a local contractor that was willing to come on site to pick up samples. We also preferred to have a laboratory with a proven record.

# **4 Performance Assessment**

# 4.1 Performance criteria

The criteria for the evaluating the performance of the Snap and RGC samplers is given in Table 18.

Table 18. Performance criteria for Snap and RGC samplers vs. low-flow sampling.

Performance Criteria	Description	Primary or Secondary
Mechanical performance of Snap Samplers	Samplers work as described without problems, reliable, ease of use, training required, etc.	Primary
Mechanical performance of Snap Samplers	Reduced time needed to sample.	Primary
Ease of use of Snap Sampler	Easy to use, number of people required to operate sampler, training required.	Primary
Mechanical performance of RGC sampler	Samplers work as described without problems, reliable, ease of use, training required, etc.	Primary
Mechanical performance of RGC sampler	Reduced time needed to sample.	Primary
Ease of use of RGC sampler	Easy to use, number of people required to operate sampler, training required.	Primary
Factors Affecting Technology Performance of Snap Sampler	Describe how technology performance is affected by operating conditions (e.g., ground water flow in wells, turbidity, temperature, etc.). Describe how matrix effects (e.g., soil type, well construction, presence of particles, pH, DO, contaminants, etc.) may affect technology performance.	Primary
Factors Affecting Technology Performance of RGC sampler	Describe how technology performance is affected by operating conditions (e.g., ground water flow in wells, turbidity, temperature, etc.). Describe how matrix effects (e.g., soil type, well construction, presence of particles, pH, DO, contaminants, etc.) may affect technology performance.	Primary

Performance Criteria	Description	Primary or Secondary
Reduced purge water with Snap Samplers	Document volume and time required for disposal of purge water for low-flow sampling	Primary
Reduced purge water with RGC samplers	Document volume and time required for disposal of purge water for low-flow sampling. Document volume discarded from RGC sampler.	Primary
Equivalent analyte recovery Snap Sampler & low-flow	According to performance criteria (statistical tests, RPDs less than 25%)	Primary
Equivalent analyte recovery low- flow samples & RGC sampler	According to performance criteria (statistical tests, RPDs less than 25%)	Primary
Equivalent analyte selectivity of Snap Sampler	Compile analyses of performance criteria for all the analytes	Primary
Equivalent analyte selectivity of RGC sampler	Compile analyses of performance criteria for all the analytes	Primary
Equivalent analyte recovery Snap Sampler & RGC sampler	According to performance criteria (statistical tests, RPDs less than 25%)	Secondary
Reliability of Snap Samplers	Breakdown of equipment, leakage from sampler; sensitivity to environmental conditions.	Secondary
Reliability of RGC samplers	Breakdown of equipment, leakage from sampler, sensitivity to environmental conditions.	Secondary
Versatility of Snap Sampler	Describe whether the technology can be used for any other application(s) and whether it can be used at other locations. If not, could it be adapted? To what extent would the technology have to be adapted so that it can be used in other settings?	Secondary
Versatility of RGC sampler	Describe whether the technology can be used for any other application(s) and whether it can be used at other locations. If not, could it be adapted? To what extent would the technology have to be adapted so that it can be used in other settings?	Secondary

Performance Criteria	Description	Primary or Secondary
Hazardous Materials Snap Sampler	Identify any hazardous materials that will remain or might be introduced by the Snap Sampler.	Secondary
Hazardous Materials RGC sampler	Identify any hazardous materials that will remain or might be introduced by the RGC sampler.	Secondary
Process Waste for Snap Sampler	Identify any process waste produced by the technology. If there is such a waste, describe its volume, any hazards that are associated with it, and how it will be handled.	Secondary
Process Waste for RGC sampler	Identify any process waste produced by the technology. If there is such a waste, describe its volume, any hazards that are associated with it, and how it will be handled.	Secondary
Scale-up constraints for Snap Sampler	Determine if there are any scale-up constraints for full-scale use.	Secondary
Scale-up constraints for RGC sampler	Determine if there are any scale-up constraints for full-scale use.	Secondary

## 4.2 Performance confirmation methods

Performance criteria, metrics, and confirmation methods that were used for this demonstration are presented in Table 19. The primary quantitative criteria included equivalent analyte recoveries, equivalent analyte selectivity, and reduced purge water volume. The primary qualitative criteria included reduced sampling time, relatively few problems encountered when using these samplers, and that these samplers were easy to use with little training. Secondary performance criteria include scale-up considerations. Chemical analyses and associated statistical methods and records from the demonstration were used to confirm whether or not the expected performance metrics were met.

Table 19. Expected performance and performance confirmation methods.

Performance Criteria	Expected Performance Metric (pre demo)	Performance Confirmation Method	Actual (post demo)
PRIMARY CRITERIA (Performance Obje (Qualitative)	ectives)		
Mechanical Performance of Snap Sampler	Few problems encountered using sampler	Records from demonstration	Future
Mechanical Performance of Snap Sampler	Reduced time needed to sample	Records from demonstration	Future
Ease of Use of Snap Sampler	Easy to use, requires little training	Records from demonstration	Future
Mechanical Performance of RGC samplers	Few problems encountered using sampler	Records from demonstration	Future
Mechanical Performance of RGC sampler	Reduced time needed to sample	Records from demonstration	Future
Ease of Use of RGC samplers	Easy to use, requires little training	Records from demonstration	Future
PRIMARY CRITERIA (Performance Obje (Quantitative)	ectives)		
Reduced purge water with passive samplers	Document purge volume and disposal time	Records from demonstration	Future
Equivalent analyte recovery for Snap Sampler & low-flow samples	Analyte concentrations equivalent between sampling methods	Statistical analyses, RPDs	Future
Equivalent analyte recovery for RGC samplers & Low-flow samples	Analyte concentrations equivalent	Statistical analyses, RPDs	Future
Equivalent analyte selectivity of Snap Sampler	Samplers can recover same analytes as low-flow sampling	Compile analyses of performance criteria	Future
Equivalent analyte selectivity of RGC samplers	Samplers can recover same analytes as low-flow sampling	Compile analyses of performance criteria	Future
SECONDARY PERFORMANCE CRITERIA (Qualitative)	<b>\</b>		
Scale-up considerations for the Snap Sampler	Determine any scale-up constraints for this sampler	Based upon records & analyses	Future
Scale-up constraints for RGC samplers	Determine any scale-up constraints for this sampler	Based upon records & analyses	Future
SECONDARY PERFORMANCE CRITERIA (Quantitative)	1		
Equivalent analyte recovery for Snap Sampler & RGC samplers	Analyte concentrations equivalent between sampling methods	Statistical analyses, RPDs	Future

Data quality procedures outlined in the project QAPP were followed for sampling and analyses. These procedures included using the EPA's low-flow purging and sampling protocol and the EPA's standard analytical methods. Equipment blanks were collected prior to their deployment in the field. To insure data validity, standard laboratory procedures for sample handling and analyses (as outlined in the QAPP) were strictly followed including the use of certified reference samples and certified reference standards. All data was reviewed by the laboratory supervisor to ensure that all calculations were correct and to detect any transcription errors. Any issues (including lack of agreement with reference samples) were to be reported to the PI immediately but there were not any incidents that needed to be reported.

Standard QC samples were taken at each site including field and laboratory duplicate samples, duplicates for spiked recoveries by the lab (to determine matrix affects including matrix spikes and matrix spike duplicates), laboratory blanks, and trip blanks. Laboratory duplicates give a measure of the precision of the laboratory and the related analytical methods. The results from the analyses of duplicate field samples provide a measure of the precision (repeatability) of the field sampling methods. Matrix Spikes and Matrix Spike Duplicates samples help identify matrix effects on spiked analytes of known quantity, as well as the laboratory's precision in recognizing matrix effects. The results of these analyses are detailed in sections 3.5.7.4 and 3.7.5.5.

Standard statistical analyses were used to evaluate the concentration data generated by each sampling method. These methods are given in more detail below.

# 4.3 Data analysis, interpretation and evaluation

Standard statistical analyses were used to determine if there were statistically significant differences between the concentrations of the inorganic analytes in samples collected using the Snap Sampler, the RGC sampler, and low-flow purging and sampling. In all cases, these analyses were conducted on an analyte-by-analyte basis. Analytes with measurable concentrations that allowed statistical analyses included As, Ca, Fe, Mg, Mn, K, and Na. In the few instances where analyte concentrations were below the detection limit, half the detection limit was used in the statistical analyses.

In instances where the data were normally distributed and the variances were homogenous, a Repeated Measures Analysis of Variance (RM-ANOVA) test was used. If the data were not normally distributed and/or the variances were not homogeneous, the data were log transformed and retested for normality and homogeneity. If the log-transformed data met the requirements for normality and homogeneity, then the log-transformed data were tested using the RM-ANOVA test. If neither the raw data nor the log-transformed data met the requirements for normality and homogeneity, then a Freidman Repeated Measures Analysis of Variance on Ranks test was used.

Filtered and unfiltered samples were analyzed separately. Specifically, analyte concentrations in the filtered Snap Sampler samples, the filtered low-flow samples, and the RGC samplers were compared. Concentrations in the unfiltered Snap Sampler samples, the unfiltered low-flow samples, and the RGC samples were also compared.

# 4.4 Findings from the field demonstration

The purpose of this field demonstration was to determine if the Snap Sampler recovered samples with equivalent concentrations of inorganic analytes to those recovered in samples collected using low-flow purging and sampling. In addition, we also wanted to examine the relationship between analyte concentrations of metals in samples collected using the Snap Sampler, low-flow sampling, and a diffusion sampler (i.e., the RGC sampler). We anticipated that the concentrations of metals in whole water samples (collected either with the Snap Sampler or low-flow sampling) would most likely be higher than concentrations in a diffusion sampler (which would be naturally filtered by the membrane) if colloidal transport was significant in these wells.

The various types of metals that were found in measurable concentrations in these wells included: Ca, Fe, Mg, Mn, K, and Na. These analytes typically occur as cations in groundwater. In addition, these wells contained measurable concentrations of As which is usually present as an anion in ground water.

Given that there were not large differences in analyte concentrations with depth in these wells, we would predict that we would not expect to find large differences between analyte concentrations in the Snap Sampler samples vs. those collected using low-flow purging and sampling.

## 4.4.1 Sampler performance and safety issues

For the Snap Sampler there was no purge water or other waste water than had to be disposed of. For the RGC sampler, there also was no purge water to dispose of but there were small amounts of residual sample water that required disposal.

Generally, the Snap Samplers performed well by triggering on demand and providing full samples. Out of the 41 samples collected, there were four instances when one of the caps did not seal properly because the o-ring did not seat properly. In instances where the o-ring was on the bottom of the sampler, there was leakage of some of the sample as it was withdrawn from the well. In two cases, there was excessive sediment in the samples; these particles may have prevented the o-rings from seating properly. Later, the laboratory discovered that two bottles had pinhole leaks in the seam and there was some loss of sample during shipping and storage. (These bottles were returned to the developer after the sampling was complete so that they could be examined. The developer has since changed the polymer that the bottles are made out of from PP to HDPE, which has better weld properties.) There also was one instance where we found the top cap of one of the samplers deployed prematurely, and there was one instance during deployment where the ball connector had pulled off the trigger line. In these instances the samplers had to be redeployed. Because there were issues with some of the samples collected, we would recommend deploying an additional bottle as insurance.

There are no moving parts on the RGC samplers so the only problems that might occur would be tearing, causing loss of the sampler or degradation of the membrane. However, no problems were encountered during this demonstration.

With respect to safety issues, there were no injuries related to using any of the three sampling technologies. Generally, there were fewer safety concerns with the passive samplers. For the RGC sampler, possible issues include spilling acid from the sample bottle, and exposure to the sample's contaminants during transfer or during disposal. There are also relatively few issues with using the Snap Sampler. These include, injury from piercing the septum (to add acid to the sample bottle), spilling acid while adding acid to the sample bottle, and exposure to the sample's contaminants if transferring the sample to another container. In contrast, for low-flow sampling there numerous safety concerns. These include electrical con-

cerns with using the sampling equipment (especially in the rain); spillage and fire hazards associated with working with gasoline and running a generator; possible burns from generator's muffler; strained or pulled muscles from moving heavy equipment in and out of the vehicle; prolonged exposure to the sample's contaminants during purging, sampling, and waste disposal; spilling acid from the sample bottles; and tripping over electrical cords.

# 4.4.2 Sampling time and personnel requirements

The sampling time for both the Snap Sampler and the RGC sampler was considerably less than that needed for low-flow sampling. We also determined that, during normal sampling events, the sampling time the Snap Sampler would be less than that for the RGC sampler. This is because only one trip to the field would be needed for the Snap Sampler whereas the RGC sampler would require two trips to the field; one to deploy the sampler and one to recover the sampler. In contrast, a new Snap Sampler can be deployed in the well at the end of a sampling event and left in the well until the next sampling event. Time savings are given in more detail in costs (Section 5).

For both the Snap and RGC samplers, sampling can be easily accomplished with one individual. While one individual can also conduct low-flow sampling, generally a field crew of two is preferred. These differences also figure into the cost of the sampling methods (see Section 5).

With respect to the training time needed to become proficient with the sampling method, the Snap Sampler required a longer training time than did the RGC sampler. For the Snap Sampler, it takes several minutes of training and some practice to become proficient. In contrast, there is not much to learn to deploy the RGC sampler. With respect to constructing the RGC samplers, the guidance on their construction was easy to follow. The only issue that we encountered was that there was no guidance about what width of dialysis tubing or diameter of support tubing to order. Also, for the size of the dialysis tubing, the manufacturer only lists the flat width of the tubing. Therefore, it is important to calculate correctly the diameter of dialysis tubing so that the support tubing will fit inside the dialysis membrane.

# 4.4.3 Analyte recovery

The findings for this study can be found in Table 20. Generally, concentrations of the analytes in the Snap Sampler were equivalent to those found using low-flow sampling.

Table 20. Findings from the field study.

Filtered Samples Unfiltered Samples							
Analyte	Well Mean Concentration (mg/L)		Untilitered Samples  Mean Concentration (mg/L)				
		Low-flow	RGC	Snap	Low-flow	RGC	Snap
	13-5045	0.097	0.16	0.12	0.16	0.16	0.16
	13-6095	0.044	0.059	0.054	0.056	0.059	0.058
	32-5020	0.074	0.15	0.053	0.15	0.15	0.15
	32-5020	0.068	0.094	0.045	0.11	0.094	0.10
As	32-5031	0.031	0.11	0.024	0.063	0.11	0.13
AS	32-5076	0.026	0.062	0.019	0.054	0.062	0.051
	32-6008	0.051	0.055	0.041	0.059	0.055	0.069
	32-6064	0.060	0.092	0.022	0.095	0.092	0.14
	32-6064	0.070	0.10	0.043	0.093	0.10	0.11
	32-6135	0.025	0.023	0.027	0.023	0.023	0.027
As	Mean	0.055ª	0.091b	0.045ª	0.086℃	0.091°	0.100°
	13-5045	69	71	70	72	71	66
	13-6095	43	43	42	42	43	41
	32-5020	230	250	230	230	250	190
	32-5020	140	130	150	150	130	150
Ca	32-5031	72	86	93	75	86	97
	32-5076	62	58	60	58	58	53
	32-6008	97	98	96	98	98	100
	32-6064	170	170	170	170	170	180
	32-6064	110	110	110	110	110	110
	32-6135	4.5	4.4	4.6	4.3	4.4	5.1
Ca	Mean	100ª	102ª	103ª	101°	102°	99.0°
	1						
Fe	13-5045	9.1	14	9.4	15	14	14
	13-6095	1.5	3.1	2.4	3.3	3.1	3.7
	32-5020	<0.05	4.4	<0.05	5.0	4.4	13
	32-5020	<0.05	2.6	0.14	3.6	2.6	4.1
	32-5031	<0.05	9.0	<0.05	4.4	9.0	20
	32-5076	<0.05	4.4	<0.05	2.3	4.4	6.3
	32-6008	<0.05	0.79	<0.05	0.62	0.79	1.4

Analyte	Well		tered Sample			tered Sample	
		Low-flow	RGC	Snap	Low-flow	RGC	Snap
	32-6064	<0.05	1.8	<0.05	1.8	1.8	4.5
	32-6064	<0.05	2.1	<0.05	1.8	2.1	2.6
	32-6135	<0.05	0.25	<0.05	0.26	0.25	4.5
Fe	Mean	1.1ª	4.2b	1.2ª	3.8°	4.2°	7.4 <sup>d</sup>
			•			•	
	13-5045	12	12	13	12	12	12
	13-6095	8.1	7.7	8	7.6	7.7	7.5
	32-5020	53	52	53	53	52	47
	32-5020	38	36	40	36	36	41
24	32-5031	18	21	22	18	21	25
Mg	32-5076	13	13	13	13	13	12
	32-6008	35	34	33	34	34	33
	32-6064	49	52	51	52	52	50
	32-6064	43	40	38	38	40	36
	32-6135	1.9	1.8	1.9	1.8	1.8	2.2
Mg	Mean	27ª	27ª	27ª	27°	27°	27°
	1	Į.					
	13-5045	8.0	7.8	7.8	7.3	7.8	7.4
	13-6095	8.0	7.9	7.8	7.9	7.9	7.7
	32-5020	0.70	0.71	0.70	0.71	0.71	0.77
	32-5020	0.43	0.44	0.49	0.46	0.44	0.54
Mm	32-5031	0.23	0.46	0.44	0.23	0.46	0.75
Mn	32-5076	0.53	0.56	0.53	0.52	0.56	0.55
	32-6008	0.22	0.22	0.21	0.22	0.22	0.22
	32-6064	0.37	0.41	0.38	0.37	0.41	0.44
	32-6064	0.20	0.21	0.21	0.20	0.21	0.21
	32-6135	0.018	0.024	0.022	0.024	0.024	0.13
Mn	Mean	1.9ª	1.9ª	1.9ª	1.8c	1.9°	1.9°
						•	
К	13-5045	2.8	2.7	2.7	2.8	2.7	2.6
	13-6095	1.6	1.6	1.6	1.5	1.6	1.5
	32-5020	8.6	8.4	8.6	8.8	8.4	8.7
	32-5020	7.1	6.4	7	7.1	6.4	7.6
	32-5031	5.3	4.6	4.8	5.4	4.6	6.8
	32-5076	4.0	3.8	3.9	3.8	3.8	4.0
	32-6008	10	9.8	10	10	9.8	10
	32-6064	11	12	11	11	12	12

Analyte	Well	Filtered Samples Mean Concentration (mg/L)			Unfiltered Samples Mean Concentration (mg/L)		
		Low-flow	RGC	Snap	Low-flow	RGC	Snap
	32-6064	9.8	9.7	9.2	9.0	9.7	8.9
	32-6135	8.2	8.4	8.3	7.9	8.4	8.2
K	Mean	6.8ª	6.7a	6.7ª	6.7°	6.7℃	7.0c
	13-5045	120	98	99	140	98	88
	13-6095	15	14	14	14	14	14
	32-5020	73	72	72	72	72	62
	32-5020	57	54	62	56	54	62
Na	32-5031	59	34	34	60	34	32
ina	32-5076	27	26	27	26	26	23
	32-6008	99	92	94	95	92	91
	32-6064	68	69	70	71	69	68
	32-6064	61	58	55	53	58	55
	32-6135	160	160	160	180	160	170
Na	Mean	<b>74</b> a	<b>68</b> <sup>b</sup>	<b>69</b> a, b	<b>77</b> °	68°	67∘

NOTE: For each analyte, there is no statistically significant difference between mean values having the same superscript letter following.

#### 4.4.3.1 Total analyte concentrations (unfiltered samples)

There were no statistically significant differences in the concentrations of these analytes between the low-flow samples vs. the RGC samples or the Snap Sampler samples with one exception, and that is the Fe levels in the Snap Sampler. We believe that exception occurred for two reasons: (1) the small pore size of (18 Å or 1.8 x  $10^{-3}\,\mu)$  of the cellulose membrane prevented all but the very smallest of colloidal particles from entering the RGC sampler and (2) the low-flow and Snap Sampler samples were whole water samples. These findings indicate that colloidal transport of this contaminant is not a predominant transport mechanism at this site.

We believe that the Fe concentrations in the Snap Sampler represented the conditions in the well at the time of sampling and are an indication of the higher levels of particulates present in the well at the time of sampling. We believe that placing the baffles and additional sampling equipment in the well (i.e., the pump, Snap and RGC samplers, and bottle weight) acted as a surge block in the well and elevated turbidity and oxygen levels (which caused oxidation/precipitation reactions to occur with the iron in the

well), and thereby falsely elevated concentrations of Fe. (When we placed the equipment in the wells, we actually heard a sound similar to a plunger in a toilet bowl.) Apparently some of the wells never fully recovered, even after leaving this equipment in the wells for two weeks.

Although we did not measure the turbidity in the Snap Sampler samples<sup>8</sup>, the initial turbidity values at the start of low-flow sampling (Table 21) indicated that, generally, turbidity was considerably less during the preliminary round of sampling than it was during the field demonstration. This supports our hypothesis that deploying all this equipment in the well elevated the turbidity. The most affected wells included 32-5020, 32-5031, and 32-5076. We discuss this in more detail in Section 4.4.3.4which provides an analysis of data on a well-by-well basis.

#### 4.4.3.2 Dissolved analytes (filtered samples)

For the filtered samples, there were no statistically significant differences between the analyte concentrations in the Snap Sampler samples and the low-flow samples for any of the analytes. There also was not a statistically significant difference between the concentrations of Ca, Mg, Mn and K in the RGC samples compared with the filtered low-flow samples. However, there was a statistically significant difference between the concentrations of As, Fe, and Na in the RGC samples and the filtered, low-flow samples; concentrations of As and Fe were higher and concentrations of Na were lower in the RGC samples. These anomalies can best be understood by comparing the concentrations in the filtered and unfiltered low-flow samples.

Table 21. Purge times and turbidity values* for low-flow sampling during the initial sampling
and the field demonstration

	Initial sampling									
Well No.	32-6064	32-6064	32-5020	32-5020	32-5031	32-5076	32-6135	13-5045	32-6008	13-6095
Pump No.	2291	2291	2269	2269	1470	2271	2270	2292	1472	1400
Purge time (minutes)	88		37		61	79	91	61	63	50
Initial turbidity	2		4		14	11	27	8	31	9
Final turbidity	1		4		11	8	20	8	32	11

<sup>8</sup> This can be done by collecting an additional sampler and then measuring the sample with a turbidity meter.

	Field demonstration									
Well No.	32-6064	32-6064	32-5020	32-5020	32-5031	32-5076	32-6135	13-5045	32-6008	13-6095
Round	1	2	1	2						
Purge time (minutes)	99	86	62	223	121	214	81	81	63	93
Initial turbidity	15	7	40	11	490	38	22	11	9	14
Final turbidity	5	4	42**	26**	11	20	6.5*	9	9	7

<sup>\*</sup> All turbidity values taken with Horiba probe unless noted otherwise. Value measured with LaMotte turbidity meter.

#### 4.4.3.3 Comparing the filtered vs. unfiltered low-flow samples

When the low-flow filtered samples were compared with the low-flow unfiltered samples, there was a statistically significant difference between the treatments for As and Fe, but not for the other cations. If colloidal transport is not responsible for these differences (as shown previously), then the filtered samples must have a falsely low bias. Since these samples were filtered in the laboratory, it is reasonable to assume that there were losses of iron due to the precipitation of hydrous iron oxides that occurred during shipping and storage (prior to filtration) and that the losses of the As anion resulted from co-precipitation with the hydrous iron oxides. Several studies (Korte and Fernando 1991; Korte et al. 1976; Jenne 1968) have shown that anions are more readily removed by iron oxides than cations, and that the most important mechanism for the accumulation of arsenic in sediment is adsorption on and coprecipitation with hydrous iron oxides (Aggett and O'Brien 1985; Aggett and Roberts 1986 [as given by Mok and Wai 1990]; Korte 1991). The findings between the filtered and unfiltered Snap Sampler samples were also similar.

Initially, we had considered using in-line filtration for the low-flow samples. However, the Snap Sampler samples could not be filtered using an inline filter, and we wanted to use the same filtration equipment for both sampling methods. We considered filtering the samples in the field using a suction or hand filtration apparatus, but were concerned that this might add more bias than simply shipping the samples to the laboratory for filtration. Given our findings, field filtration of the samples would have been prudent because the sample handling clearly affected filtered concentrations of both Fe and As.

<sup>\*\*</sup> Issues with meter and with particles collecting in flow-through cell.

#### 4.4.3.4 Well-by-well comparisons using unfiltered sample data

While the statistical analyses clearly indicate there is no consistent (significant) bias associated with using the Snap Sampler when compared with low-flow purging and sampling (for any of the analytes except unfiltered iron), we also examined the unfiltered data on a well-by-well basis to see if there were any wells where there appeared to be a large difference in the results for the different sampling methods.

The flow testing showed that for four of the wells (32-6008, 32-6064, 13-6095, and 32-5076), there was a significant contribution from one portion of the well under pumped conditions, but there was no vertical flow under ambient conditions. We expected that we might find poor agreement between the concentrations in the Snap Sampler vs. the pumped samples for those wells if there also was a concentration gradient in those wells. For two of those wells, 32-5076 (10-ft screen) and 32-6008 (14-ft screen), there was no apparent concentration gradient with depth, so we would not expect any difference with these wells. For the other two wells, there was a concentration gradient for some analytes with depth. For well 13-6095 (10-ft screen), the concentrations of As and Fe were slightly higher ( $\sim$ 2x) in the shallow portion of the well screen. The findings for well 32-6064 (10-ft screen) were similar, with slightly larger differences in concentrations (~3x for As and 10x for Fe). However, there was excellent agreement between the analyte concentrations in the low-flow samples vs. the Snap Sampler samples in those wells.

In contrast, the wells with perhaps the poorest agreement between the concentrations in the unfiltered samples taken with the Snap Sampler vs. low-flow sampling were well numbers 32-6135 and 32-5031. For well 32-6135, in the Snap Sampler, the concentration of Fe was ~10x higher and the Mn concentration was ~5x higher. For Well 32-5031 in the Snap Sampler, there were higher concentrations of three analytes (As, Fe, and Mn); specifically, As was 2x higher, Fe was 5x higher, and Mn concentrations were ~3x higher. Both of these wells are stainless steel wells. (The other six wells were made with PVC casing and screen.) Although we might expect Fe and Mn concentrations to be higher in stainless steel wells as a result of leaching (Parker, Hewitt, and Jenkins 1990; Hewitt 1989, 1992, 1994), arsenic is not a component of stainless steel so there is no reason to expect elevated concentrations of As in these wells. Thus, we suspect that much of these elevated concentrations of analytes resulted from higher turbidities in these wells. Higher turbidities may be the result of installation of all the

sampling equipment in the well (as mentioned previously), from poor well-construction methods, or from degradation (corrosion) of the well screens, resulting in an increased slot size. (The improper selection of the slot size of the screen and/or the grain size of the filter pack can result in larger fines entering a well.) We were not able to successfully redevelop well 32-6135. Thus, this may be an example of a well with an elevated native turbidity that resulted from poor well construction design or degradation of the screen. In contrast, well 32-5031 appears to have been dramatically affected by the installation of all the equipment in the well; the initial low-flow turbidity reading for this well was 35x higher in this sampling event than it was in the preliminary sampling round (Table 21). As mentioned previously, agitating the well can result in coprecipitation of the As, which would explain the elevated concentration of this analyte in this well.

Other wells where there were elevated Fe levels included numbers 32-5076, 32-5020, and 32-6064. These wells also appear to have been affected by the installation of the sampling equipment in the well as the initial turbidity reading for these sampling events were 2–10x higher than during the preliminary sampling round (Table 21).

Generally, in the RGC samplers concentrations of Fe were similar to those found in the low-flow samples, except for wells 32-5031 and 32-5076, where the concentrations of Fe were elevated but not as much as the concentrations found in the Snap Sampler. Concentrations of As and Mn were also similarly elevated in the RGC samples from well 32-5031. These data support the hypothesis that the Snap Sampler concentrations were elevated because of higher turbidities in these wells.

In contrast to the occasionally higher concentrations of other analytes found in the Snap Sampler, lower concentrations of unfiltered Na were found in the Snap Sampler samples collected from wells 32-5031 and 13-5045, where concentrations were approximately one-half those found in the low-flow samples. This may be because low-flow pumping brought in more saline water from the surrounding estuary. These were the two shallowest wells.

Again, for most of the analytes from most wells, there was close agreement between concentrations of inorganic analytes in both the Snap Sampler samples and the low-flow samples. The one analyte where we did observe a statistically significant difference was unfiltered Fe where the concentrations were higher in the Snap Sampler. These levels appear to reflect the turbidity of the well at the time of sampling and for most of the wells it appears that the disturbance caused by adding the baffle and other sampling equipment to the well was responsible for these elevated levels.

Subsequent studies should examine: (a) whether the Snap Sampler raises turbidity in wells under normal deployment conditions (i.e., without the baffle and the other equipment used this study) (b) if so, which types of wells are affected, and (c) whether analyte concentrations in shallow wells are more apt to be affected by the sampling method (i.e., pumping vs. passive).

# **5** Cost Results

## 5.1 Cost reporting

The cost models that were used for estimating the cumulative quarterly sampling costs over a 10-year period are given in Table 22 for the Snap Sampler, Table 23 for the low-flow purging and sampling, and Table 24 for the RGC sampler. These models include the costs associated with initial startup, the materials needed for sampling (including both equipment and consumables), equipment installation, labor costs, and inflation.

Table 22. Cost model for the Snap Sampler: 10-yr period, with quarterly sampling.

Cost Element	Data Tracked During the Demonstration	Details	Cost (\$)
Initial Startup	Planning fieldwork, equipment, supplies, and personnel	Project Technician (1)	\$60/hr
Materials	Equipment & consumables	Snap Sampler lines, holders, trigger mechanism, bottles, etc.	purchase price
	First-time sampler deployment	Project Technician (1)	\$60/hr
Installation	Materials	Supplies	purchase price
Quarterly	Quarterly sampling, redeployment of new samplers, & clean up	Project Technician (1)	\$60/hr
Sampling	Materials	Replacement sampler bottles, etc.	purchase price
		After Year 1, no inflation	
	Total Costs	After 5 years, no inflation	
		After 10 Years, no inflation	
	Cumulative Costs, assuming OMB's 2.2% annual inflation average:	Yearly sampling costs + cumulative inflation	Total Costs
	After Year 1		
	After Year 2		
Long-term Monitoring	After Year 3		
lee	After Year 4		
	After Year 5		
	After Year 6		
	After Year 7		
	After Year 8		
	After Year 9		
	After Year 10		

Table 23. Cost model for low-flow sampling: 10-yr period, with quarterly sampling.

Cost Element	Data Tracked During the Demonstration	Details	Cost (\$)
Initial Startup	Planning fieldwork, equipment, supplies, personnel, etc.	Project Technician (1)	\$60/hr
Materials	Equipment & consumables	Bladder pumps, tubing, controller, generator, air compressor, air hose, etc.; Purge parameter equipment, calibration standards, etc.; Decon equipment.	Purchase price
		Project Technician (2)	\$120/hr
Installation	First-time equipment deployment	Supplies	Purchase price
	Quarterly sampling & clean up: including field set up, purge	Project Technician (2)	\$120/hr
Quarterly Sampling Costs	stabilization, sampling time, sample preparation, decon of equipment, purge water disposal, breakdown of field site	Supplies, standards for purge parameters, DI water for decon, gasoline, etc.	Purchase price
		After Year 1	
	Total costs, no inflation	After Year 5	
		After Year 10	
	Cumulative Costs, assuming OMB's 2.2% annual inflation avg.	Yearly sampling costs + cumulative inflation	Total Costs
	After Year 1		
Long-term Monitoring	After Year 2		
	After Year 3		
	After Year 4		
	After Year 5		
	After Year 6		
	After Year 7		
	After Year 8		
	After Year 9		
	After Year 10		

**Data Tracked During** Cost Element Details Cost (\$) the Demonstration Planning fieldwork, equipment, Project Technician (1) \$60/hr **Initial Startup** supplies, personnel, etc. Equipment & consumables Purchase Membrane, support & (each quarter) protective mesh, etc. price Materials One time equipment and Weights Purchase consumables price Sampler construction (ea. quarter) Project Technician (1) \$60/hr Sampler deployment (each quarter) Project Technician (1) \$60/hr Supplies (ice for samplers, Purchase Installation nitrogen for degassing price samplers, etc.) Sampler retrieval (second trip ea. Project Technician (1) \$60/hr quarter); includes: retrieval of Sampler sampler, sample transfer, sample Retrieval labeling, site clean up, disposal of wastes. **Total Costs** After Year 1 After Year 5 After Year 10 Cumulative Costs, assuming OMB's Yearly sampling costs + 2.2% annual inflation average cumulative inflation **Total Costs** After Year 1 After Year 2 Long-term After Year 3 Monitoring After Year 4 After Year 5 After Year 6 After Year 7 After Year 8 After Year 9 After Year 10

Table 24. Cost model for the RGC sampler: 10-yr period, with quarterly sampling.

#### 5.2 Cost drivers

We concluded that the following items comprise the major cost drivers for the Snap Sampler. (Please note that all the values used in this analysis are adjusted for inflation.)

• **The number of analytes.** The more analytes that need to be sampled, the more Snap Sampler bottles that will be needed, which drives up the cost of sampling. As an example, if we had also sampled for

VOCs, that would have required adding at least two more samplers to the string of samplers and purchasing two additional VOC bottles per well (plus 10% QA/QC samples). The estimated savings over 10 years using only Snap Sampler for the inorganic analytes would have been 67%, for an estimated cost of ~\$296K. By contrast, the estimated cost savings would have been only 57% if one had monitored for both VOCs and inorganics, for an estimated 10-year cost of \$390.5K.

- **Sample volume requirements.** Large sample volume requirements can also increase the number of sampler bottles used. As an example, if we had to sample for low levels of explosives at this site (instead of inorganics) then we would need 500 mL of sample. To do this, we would need four 125-mL bottles, rather the two bottles used in this study. The cost savings in this case would be similar to the previous example, 57% for an estimated 10-year cost of ~\$390.5K.
- **Depth of the sampling interval.** At this site, the wells were relatively shallow and a manual trigger line could be used. At one of our other sites, the former McClellan AFB, the wells were much deeper and required an electronic trigger. However, the electronic trigger is a one-time cost that is fairly modest when compared with the total cost of sampling. This cost would be divided by the anticipated length of time for long-term monitoring (LTM) and the number of sampling events each year.
- **Reconditioning of the wells.** It is not known how often the wells will have to be redeveloped or reconditioned. Given time and financial constraints, this is often an issue that currently is disregarded by sampling teams using conventional sampling methods. However, even if one assumed that the wells sampled with the Snap Sampler will need to be reconditioned every 5 years, the estimated cost savings from using this technology would still be over 50%. The projected long-term cost would be ~\$422K, with an estimated cost savings of 53.5% over low-flow sampling (with no well conditioning).
- **Replacing Snap Sampler hardware.** Given the materials used in the Snap Sampler (mostly rigid plastics), we would not anticipate that the equipment would require replacement during the 10-year deployment period. However, even if the equipment had to be replaced every 5 years, the estimated 10-year monitoring cost using the Snap Sampler would be ~\$375K, and the cost savings would still be substantial at 58% (vs. the initial cost savings of ~\$296K, for an estimated cost savings of 67%).

# 5.3 Cost analysis

The cost analyses for each of these sampling technologies were calculated over a 10-year period, based upon the costs incurred at this site, but extrapolated for a typical site that consisting of 50 monitoring wells. The following considerations were included: capital costs; startup costs, opera-

tions and maintenance costs, and waste disposal costs (i.e., the time needed to take wastewater to the disposal facility on site). To perform the cost comparisons between the three sampling methods — low-flow purging and sampling, the Snap Sampler, and the RGC sampler — the following assumptions about this site were made.

- The number of monitoring wells at this site was assumed to be 50.
- The wells are to be sampled quarterly for a period of 10 years.
- The mean sampling depth used will be the same as that of the 10 wells in this demonstration (36 ft).

Other assumptions made for the cost analyses include the following.

- For low-flow sampling, the field crew would consist of two people.
- Only one individual would be needed to collect samples using a Snap Sampler or a RGC sampler.
- The analytes of interest would be only those examined in this study.
- The minimum sample volume needed was determined by the laboratory.
- The RGC samplers would be constructed by the field technician.
- New Snap Sampler bottles would be used at each deployment (rather than cleaning and reusing bottles).
- An additional trip to the field would not be necessary to deploy the Snap Samplers since they would be routinely re-deployed after each sampling event.
- An additional trip to the field would be necessary to deploy the RGC samplers because of their relatively short shelf life (in-situ).
- No initial well conditioning would be needed for low-flow sampling at the beginning of a 10-year sampling program.
- Initial well conditioning would be needed for the Snap Sampler and the RGC sampler at the beginning of a 10-year sampling program.
- Dedicated equipment would be used in all wells, including pumps for low-flow sampling.
- There would be no replacement of equipment during the 10 years (such as bladder pumps or Snap Sampler bottle holders).
- There would be no periodic redevelopment of the wells during the 10 years.
- There would be no economy of scale factored into sampler costs of either the Snap Sampler or RGC samplers.

All cost values being compared in this discussion allowed for an annual inflation rate of 2.2%. This analysis will be given in more detail in the related Cost and Analysis report associated with this project.

Annual

Sampling

The total estimated cost for sampling 50 wells quarterly for 10 years using low-flow sampling was projected to be  $\sim$ \$907.6 K (Table 26). As mentioned previously, this assessment is based upon a two-person field crew. The estimated cost for the same number of sampling events using the Snap Sampler came to \$296.1 K, or a 67% cost savings (Table 25). The estimated cost for using the RGC sampler at this site was \$257.9 K a cost savings of 71% (Table 27). For both of the Snap Sampler and the RGC sampler, this assessment was based upon a field crew of one. The cost savings would have been more for the RGC sampler if a second trip to the field was not needed. Clearly, greater savings could be achieved by using a similar diffusion sampler that has a more resilient membrane.

One can see that the number of field technicians and the sampling time associated with low-flow sampling are major reasons for the cost savings associated with passive sampling methods. As an example, if we estimate that the field crew for low-flow sampling consisted of one individual and it took that person 1.5 times the time it takes two to sample, we estimate that the cost of low-flow sampling at the site would be  $\sim$ \$491.9 K or  $\sim$ 45% less. However, even using this lower cost estimate for low-flow sampling, the cost savings with the Snap Sampler would still be substantial,  $\sim$ 39%.

On a per-sample basis, we estimate that over 10 years, the cost per sample at this site would be \$187.70 with low-flow sampling. In contrast, we estimate that the per-sample cost for the Snap Sampler would be \$62.40, and for the RGC sampler it would be \$53.95 (without adding in inflation).

Cost Element	Data Tracked During The Demonstration	Details	Cost (\$)
Initial Startup	Planning fieldwork, equipment, supplies, and personnel	Project Technician, 64 hr	3,840
	Well reconditioning	Contract	37,500
	Well reconditioning	Subtotal	41,340
Material	Equipment- non-consumables	Snap Sampler equipment	23,405
Waterial	Equipment non-consumables	Subtotal	23,405
		Project Technician, 36 hr	2,160
Installation	First-time sampler deployment	Supplies	2,962
		Subtotal	5,122

Quarterly sampling for remainder of

first year

Project Technician, 200 hr

Sampler bottles, other sply.

Subtotal

12,280

8.344

20.624

Table 25. Projected monitoring costs using the Snap Sampler for 10 years.

Cost Element	Data Tracked During The Demonstration	Details	Cost (\$)
		After Year 1	88,859
	Total Costs, no inflation	After Year 5	171,355
		After Year 10	274,475
	Cumulative Costs, assuming OMB's 2.2% annual inflation average	Yearly sampling costs + inflation	Total Costs
	After Year 1		88,859
Long-term	After Year 2	21,078	109,937
Monitoring	After Year 3	21,541	131,478
	After Year 4	22,015	153,494
	After Year 5	22,500	175,993
	After Year 6	22,995	198,988
	After Year 7	23,501	222,488
	After Year 8	24,018	246,506
	After Year 9	24,546	271,052
	After Year 10	25,086	296,138

Table 26. Projected monitoring costs, using low-flow sampling for 10 years.

Cost Element	Data Tracked During the Demonstration	Details	Cost (\$)
Initial Startup	Planning equipment, supplies,	Project Technician, 64 hrs	3,840
	fieldwork, and personnel	Subtotal	3,840
		Bladder pumps, tubing, cable, controller	30,435
	Dadicated consuling convinue at 0	Purging equipment	6,365
Material	Dedicated sampling equipment & supplies	Gas-powered generator	1,100
		Other equipment, tools, & supplies	1,195
		Subtotal	39,095
		Project Technicians, 88 hrs	5,280
Installation	Deploy pumps	Decon supplies	15
		Subtotal	5,295
		Project technicians, 836 hrs	74,460
Annual Sampling	Sampling	Supplies	3,306
		Subtotal	77,766

Cost Element	Data Tracked During the Demonstration	Details	Cost (\$)
		After Year 1	125,996
	Total Costs, no inflation	After Year 5	437,060
		After Year 10	825,890
	Cumulative Costs, assuming OMB's 2.2% annual inflation avg.	Yearly bottles and sampling costs + cumulative inflation	Total Costs
	After Year 1		125,996
1	After Year 2	79,477	205,473
Long-term Monitoring	After Year 3	81,225	286,698
	After Year 4	83,012	369,710
	After Year 5	84,839	454,549
	After Year 6	86,705	541,254
	After Year 7	88,613	629,867
	After Year 8	90,562	720,429
	After Year 9	92,554	812,983
	After Year 10	94,591	907,574

Table 27. Projected monitoring costs, using the RGC sampler for 10 years.

Cost Element	Data Tracked During the Demonstration	Details	Cost (\$)
Initial Charton	Planning fieldwork, personnel, ordering	Project Technician, 50 hr	3,000
Initial Startup	Well reconditioning	Contract	37,500
	Well reconditioning	Subtotal	40,500
		Project Technician, 25 hr	1,500
   Material	Purchasing and construction, personnel	Reusable equipment, supplies	949
Iviaterial		Sampler materials, expendable	529
		Subtotal	2,978
	First time a second or deadles were at 0	Project Technician, 21 hr	1,260
Installation	First-time sampler deployment & waste disposal	Expendable supplies	289
		Subtotal	1,549
Sampler Retrieval	Retrieve samplers	Project Technician, 22 hr	1,320
Camplet Nettleval	Remove sumplers	Subtotal	1,320

Cost Element	Data Tracked During the Demonstration	Details	Cost (\$)
		After Year 1, no inflation	61,041
	Total Costs	After 5 years, no inflation	139,409
		After 10 Years, no inflation	237,369
	Cumulative Costs, assuming OMB's 2.2% annual inflation average.	Yearly sampling costs + cumulative inflation (\$)	Total Costs
	After Year 1		61,041
	After Year 2	20,023	81,064
Long-term Monitoring	After Year 3	20,464	101,528
Montoning	After Year 4	20,914	122,441
	After Year 5	21,374	143,815
	After Year 6	21,844	165,659
	After Year 7	22,325	187,984
	After Year 8	22,816	210,800
	After Year 9	23,318	234,117
	After Year 10	23,831	257,948

# **6 Implementation Issues**

Although this demonstration and our previous studies (Parker et al. 2007) have shown that there does not appear to be any consistent bias associated with using the Snap Sampler for most organic and inorganic analytes, there were a few issues raised in this study that should be mentioned. The first is the applicability of using an equilibrated-grab sampler, such as the Snap Sampler, for collecting samples for total Fe and possibly other reactive species such as arsenic. Although it appears that elevated Fe concentrations resulted from an elevated turbidity in the wells that resulted from the installation of all the sampling equipment in the well, subsequent studies will need to examine whether the Snap Sampler raises turbidity in wells under normal deployment. Another issue that should be examined in subsequent studies is whether analyte concentrations in shallow wells are more apt to be affected by the sampling method, especially where there may be a gradient in concentrations, such as sodium and chloride concentrations near a marine environment.

#### 6.1 Environmental checklist

A survey sent to the ITRC's state-level points of contact (POCs) confirmed that there are some regulatory barriers (statutes, regulations, or guidance) that either prohibit or impede the use of passive sampler technologies (ITRC 2007). Of the 16 states responding to the survey, 25% believed their state prohibited the use of passive sampling technologies because they required either three-well-volume purging or low-flow purging and sampling. Other states require that the wells be purged, which also precludes using passive sampler technologies. However, while all states appear receptive, many request comparison studies to verify a passive sampler's reliability. New Jersey was the only responding state that has published guidance on using a specific passive sampling technology for sampling groundwater.

# 6.2 Other regulatory issues

In addition to participation by the principals involved in sampling at this site (the U.S. EPA Region 1 and NH DES), the PI and four of the project's team members were members of the ITRC Diffusion Passive Sampler

Team (R. Willey, D. Gronstal, S. Britt, and T. Imbrigiotta). The passive sampler team has been proactive in promoting various passive sampling technologies. In 2006, they published an overview document on 14 passive sampling technologies, including the Snap Sampler and the RGC sampler (ITRC 2006). Subsequently, the team published a protocol document on the use of five passive samplers, including the Snap and RGC samplers (ITRC 20007). This document provides guidance on (a) how to deploy and collect samples using these samplers, and (b) the advantages, applicability, and limitations of these technologies. Both of these documents are available free of charge on the ITRC Web site. Since 2007, the ITRC also has provided a free Internet training class on the use of these devices, with the total number trained over 1,400 (as of July 2009).

In early 2009, Ms. Parker and other colleagues in the sampling arena began drafting an ASTM standard on passive sampling (as part of D.18.21.04 on sample collection for ground water monitoring). Presumably, this document will be ready for initial sub-committee ballot in early 2011.

#### 6.3 End-user issues

Federal, state, municipal and tribal regulators, environmental consultants, the DoD and the Department of Energy (DOE) are all potential end users of this technology. As mentioned previously, the ITRC passive sampling team has been proactive in educating interested parties about passive sampling. Participants in the free Internet training on these samplers have included individuals from all of the end-user groups listed. The team believes that many of the user's concerns and decision-making factors have been addressed by the ITRC's documents and Internet training.

Snap Samplers are commercially available, and off-the-shelf devices were used in this demonstration. However, there have been some modifications to this the equipment as a result of this demonstration, and there may be additional changes that result from our next demonstration. The electronic trigger was developed with our next demonstration site in mind because of the depth of those wells (100 to 200 ft bgs). Publication of an ITRC Technical Regulatory document on passive sampling and the availability of ITRC training on passive samplers is expected to increase demand for this sampler. This presumably will drive down the cost of the sampler.

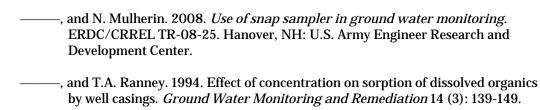
The RGC sampler currently is not commercially available, but (as of June 2009) a firm<sup>9</sup> is considering manufacturing this device. The publication of an ITRC Technical Regulatory document and the availability of Internet training presumably will facilitate broader use of this device. If the sampler becomes commercially available and is widely used, the price of this sampler also presumably would come down.

<sup>9</sup> Columbia Analytical of Kelso, WA (manufacturer of the PDB and RPP samplers).

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# **Acronyms and Annotations**

Å Angstrom

AFB Air Force Base

ANOVA Analysis of Variance test

As Arsenic

ASTM American Society for Testing and Materials (now known as

**ASTM International)** 

BFSA Bulk Fuel Storage Area

bgs below ground surface

BRAC Base Realignment and Closure

BTEX Benzene, Toluene, Ethylbenzene, Xylene

Ca Calcium

Cd Cadmium

CERCLA Comprehensive Environment Response Compensation &

Liability Act

Cr Chromium

CRREL Cold Regions Research and Engineering Laboratory

DI deionized water

DO Dissolved Oxygen

DOE U.S. Department of Energy

DoD U.S. Department of Defense

EPA U.S. Environmental Protection Agency

**EPASW EPA Office of Solid Waste** 

ERDC U.S. Army Engineer Research and Development Center

ERDC-EL-MS ERDC Environmental Laboratory- Vicksburg

ERDC-EL-EP ERCDC Environmental Laboratory- Omaha

Fe Iron

FFA Federal Facility Agreement

ft foot

ft bgs feet below ground surface

gal gallon

**GPM** Gallons per Minute

HDPE High Density Polyethylene

ICP Inductively Coupled Plasma

ICP/MS Inductively Coupled Plasma Mass Spectrometry

IRP Installation Restoration Plan

ITRC Interstate Technology and Regulatory Council

K Potassium

\$K thousand dollars

LS Lower Sand

LTM Long-term monitoring

MCL Maximum contaminant level

MCS Marine clay and silt

Mg Magnesium

mL milliliter

Mn Manganese

MS Matrix spike sample

MSD Matrix spike duplicate sample

mXYL *m*-Xylene

Na Sodium

NELAC National Environmental Laboratory Accreditation

Conference

NH DES New Hampshire Department of Environmental Services

Ni Nickel

NJDEP New Jersey Department of Environmental Protection

NPL National Priorities List

NTU Nephelometric turbidity units

ORP Redox potential

OSHA U.S. Occupational and Safety Health Administration

PAHs Polycyclic aromatic hydrocarbons

Pb Lead

PCE Tetrachloroethylene

PDB Polyethylene Diffusion Bag sampler

PE Polyethylene

pH measurement of acidity

PI principal investigator

POC points of contact

PP Polypropylene

ppb parts per billion

ppm parts per million

psi pounds per square inch

PTFE polytetrafluoroethylene

QA quality assurance

QAPP Quality Assurance Project Plan

QC quality control

RDX cyclotrimethylenetrinitramine

RGC regenerated cellulose

RM-ANOVA Repeated Measures Analysis of Variance test

RPD Relative Percent Difference

RPP Rigid Porous Polyethylene sampler

S Sulfur

SS Stainless steel

TCE Trichloroethylene

TDS Total Dissolved Solids

TNT Trinitrotoluene

US Upper Sand

USACE United States Army Corps of Engineers

UST underground storage tank

VOA volatile organic analyte

VOC volatile organic compound

Zn zinc

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**Date** 

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# Appendix A: Sampling Methods Supporting the Experimental Design

The Interstate Technology and Regulatory Council (ITRC). 2006. *Technology Overview of Passive Sampler Technologies*. The Diffusion Sampler Team of the Interstate Technology and Regulatory Council, 444 North Capitol Street, NW, Suite 445, Washington, DC 20001. Available at <a href="http://www.itrcweb.org/documents/DSP\_4.pdf">http://www.itrcweb.org/documents/DSP\_4.pdf</a>

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# Appendix B: Analytical Methods Supporting the Sampling Plan

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# **Appendix C: Quality Assurance Project Plan** (QAPP)

## C.1. Purpose and scope of the plan

The objectives of this demonstration are to compare concentrations of inorganic analytes in samples collected from ground water monitoring wells by using several sampling methods. Analytes will include non-metals, transition metals, alkaline earth metals, alkali metals, and a metalloid. Sampling methods will include low-flow purging and sampling, the Snap Sampler, and other passive diffusion samplers. Specifically for this site, samples to be taken with the Snap Sampler will be compared with samples taken using the RGC sampler and a dedicated ¾-in. diameter bladder pump. Because of the number and size of the samplers installed in each well, larger diameter wells (4-in. and 6-in.) will be needed for this demonstration. Statistical analyses will be used to determine if a statistically significant difference exists between the concentrations of samples collected using the various sampling methods.

# C.2. Quality assurance responsibilities

With respect to ensuring the integrity of the demonstration and the quality of the samples, Louise Parker, Nathan Mulherin, Sandy Britt, Richard Willey, Thomas Imbrigiotta, and the contract laboratory POC will have the following responsibilities.

Louise Parker (CRREL) will oversee all aspects of this project, direct the demonstration in the field including all the sampling events, serve as the QA Officer, review and analyze all data, and serve as primary author of the report.

Nathan Mulherin (CRREL) will be the primary field technician. He will interact with the regulators and site manager prior to the demonstration, make certain that all equipment is operational prior to deployment, conduct all preliminary sampling and develop any wells that need redevelopment, and be responsible for sending all the samples to the laboratory and filling out the chain of custody forms.

Sandy Britt (ProHydro) will review the draft plan, categorize the hydraulics in the wells prior to sampling, and be present on site during the demonstration to address any problems with the Snap Sampler.

Thomas Imbrigiotta (USGS) will review the draft plan and provide guidance on the construction, storage, and use of the RGC sampler.

Richard Willey (U.S. EPA Region 1) will review the draft plan, provide guidance throughout the demonstration, and review the final report.

The contract lab POC will have all data oversight responsibilities to ensure that samples are analyzed within the holding time, that all calibrations are not suspect, and that analyses agree for standard reference samples.

## C.3. Data quality parameters

To insure data validity, standard laboratory practices for analyses will include the following:

- receiving, log-in, and storage of field samples
- chain-of-custody documentation
- standards preparation and analysis
- Instrument calibration
- instrumentation QC
- duplicate field samples
- matrix spike samples
- field and laboratory blanks

Standard QC samples will be taken at each site, including laboratory and field duplicates, duplicates for spiked recoveries by the lab (to determine matrix effects), and trip blanks.

Trip blanks will be prepared by the contract laboratory using analyte-free reagent water. Trip blanks will be handled, transported, and analyzed using identical procedures as those used for the other groundwater samples. Equipment blanks will be collected from samplers and pumps that have been deployed in DI water for 10 days.

Duplicate field samples will be collected from 10% of the total number of samples. Duplicate samples will be obtained by using all three sampling methods (low-flow, Snap, and RGC). The results from these analyses will

provide a measure of the precision (repeatability) of the field sampling methods.

Duplicate samples for spiked recoveries will be collected for 5% of the total number of samples. These samples will be collected for the purposes of preparing Matrix Spikes (MS) and Matrix Spike Duplicates (MSD). They will be identified with the suffixes MS and MSD on the Chain-of-Custody Forms. These samples will help identify matrix effects on spiked analytes of known quantity, as well as the laboratory's precision in recognizing matrix effects.

Labels on the sample bottles will be marked with a water-insoluble marker. They will be given an identification number, and marked with the time, date, initials of the sampling individual, and whether they samples are to be filtered or not. All information about each sample also will be recorded in the (bound) green lab field book. Each sample bottle will be placed in a zipper-lock plastic bag. Samples will be stored on ice in a cooler until they are delivered to the analytical laboratory.

When the samples are ready to be sent to the contract lab, the cooler will be packed with fresh ice. A Chain-of-Custody Form will be signed, placed in a zipper-lock plastic bag, and sealed; the bag will be placed inside the cooler; and the cooler will be sealed with tape and a Chain-of-Custody Seal (in a manner that the seal must be destroyed before accessing the cooler). The cooler will then be shipped to the laboratory by overnight express (or equivalent) delivery.

Certified reference samples will be used by the laboratory to ensure proper calibration and thus accuracy of the analyses. One out of 40 samples will be a certified reference sample (2.5%). One out of 20 samples will be a calibration standard (5%).

# C.4. Calibration procedures, quality control checks, and corrective action

Five percent of the samples will be analyzed in duplicate, to give a measure of the precision of the various analyses.

The analytical laboratory will use standard U.S. EPA protocols for calibrating the analytical instrumentation including: calibration curves with a minimum of three standards at different concentrations, internal and ex-

ternal standards, and analyses of equipment blanks. Certified reference samples will be used by the laboratory to ensure proper calibration and thus accuracy of the analyses. All reference samples should agree within  $\pm 20\%$  with known concentrations.

All data will be reviewed by a second analyst (or supervisor), using procedures that ensure all calculations are correct and detect any transcription errors. Any issues (including lack of agreement with reference samples) are to be reported immediately to the PI.

### **C.5. Demonstration procedures**

There will be 10 sampling events and the well water will be analyzed for inorganic analytes. Specific analytes will include As, Ca, Fe, Mg, Mn, K, and Na. For each well, samples will be collected using the Snap Sampler, low-flow purging and sampling (U.S. EPA Region 1 1996), and the RGC sampler. Two sets of samples will be collected; one set of the samples will not be filtered (i.e., will be whole-water samples) and the other set will be filtered.

The Snap and RGC samplers will be deployed at the same depth in the well as the bladder pump (or dedicated tubing for a peristaltic pump) that will be used for low-flow sampling. Two Snap Samplers will be deployed in tandem in each well, one just above the pump intake and one just below the pump intake The samplers will be left in the well for 10 days prior to sampling.

Tentatively, 12 4-in. (or 6-in.) diameter monitoring wells have been selected as potential monitoring wells for this demonstration. Ten wells to be used in this demonstration will be selected from these 12 wells. Prior to selecting the final wells, the site geology will be reviewed and the well hydraulics will be determined for each of the wells to determine the flow patterns in the wells. In addition, all the prospective wells will be sampled prior to conducting the demonstration using low-flow sampling. This is necessary to determine (1) whether the wells have analyte concentrations that are within the desired range, (2) whether any of the wells need redevelopment prior to starting this project, and (3) whether draw down occurs in any of the wells at the sampling rate. In order to evaluate these passive and active sampling systems, it is important that all wells used in this demonstration perform as they were designed. Total depth of the wells will be measured and compared with construction diagrams to determine

if the wells have silted in. Wells that have silted in or have high turbidity levels will be redeveloped prior to starting the demonstration. In addition, two Snap Sampler samples will be collected ( $\sim 5$  ft apart) to determine if there is any contaminant stratification in these wells.

All the bladder pumps will be cleaned prior to installing them in the well. Equipment blanks will be taken prior to deployment to verify there is no leaching of analytes of interest. The length of the suspension lines for the diffusion samplers and the trigger lines will have to be determined exactly, so that the samplers can be deployed at the desired depths in the well (especially with respect to the intake of the bladder pump). The RGC samplers will have to be constructed within a week of the project. The equipment used to monitor the purge parameters will be checked a month before we begin the project and again the week before we go in the field.

### C.6. Calculation of data quality indicators

According to the contract, the laboratory will have in place procedures for demonstrating proficiency of the analytical method for each analyte. The relative percent difference (RPDs) between the laboratory's values for certified reference samples and the known values will be calculated using the same formula given previously in Section 3.5.7.5

# C.7. Performance and system audits

If the contract laboratory is unable to meet the terms of the contract, a second (back-up) laboratory will be selected at the time the contract is awarded.

# C.8. Quality assurance reports

This data will be generated from two sampling events, (i.e., two data sets). The first set of data will be the preliminary data from the 12 candidate wells. The second set of data will be the results from the demonstration comparing the three sampler types in the 10 wells. We anticipate two sets of reports from the laboratory; one after the preliminary sampling is completed and the second after the demonstration is complete. Each report will contain the information on the following: (a) sample preparation and analysis procedures, (b) instrument standardization, (c) sample data, precision and bias, (d) detection and report limits, and (e) results from all

QA/QC analyses including certified references samples and laboratory duplicates.

Laboratory reports will include all information used in calculations, (e.g., raw data, calibration files, tuning records, results of standard additions, interference check results, and blank or background correction protocols). This will allow the data to be reconstructed if need be.

#### C.9. Data format

All field data will be written in a bound, green notebook. It will be written in ink, dated, and initialed or signed by the person making the entry.

Data from the laboratory will be delivered in electronic form (a Microsoft Excel spreadsheet) in a format suitable for easy data analyses (as specified by ERDC-CRREL in the laboratory contract). Any change in automated data entries should not obscure the original entry. Updated entries should also indicate the reason for the change, the date, and the person responsible for making the change. Back-up copies of all data submitted by the contract lab will be kept.

## C.10. Data storage and archiving procedures

The data will be available as an Appendix in the final report, and that report will be available electronically on the CRREL Web site. Nate Mulherin (CRREL) will keep electronic copies of all data reports from the contract lab and records of all correspondence and other documents between CRREL and the contract lab that relate to interpretation and evaluation of the data. In addition, Mr. Mulherin will keep the green book that will be used to document everything done in the field. Ms. Parker will keep an electronic copy of the interim and final report on a CD-ROM.

# **Appendix D: Health and Safety Plan (HASP)**

(Available on request.)

# Appendix E: Data Summaries for the Second Laboratory Study.

Table E1. Recovery of the cations in the second laboratory study.

Sample	Ca	a	К		Ma	g	М	n	Na	
24-hr	Control	Snap	Control	Snap	Control	Snap	Control	Snap	Control	Snap
Mean concentration (mg/L)	19.4	19.1	42.5	42.7	8.5	8.3	36.1	35.5	47.0	46.6
% recovery of Snap Sampler		98.7		100.4		97.4		98.3		99.2
% RSD	1.1	0.7	2.0	1.5	0.6	0.5	0.0	0.7	0.5	0.1
48-hr	Control	Snap	Control	Snap	Control	Snap	Control	Snap	Control	Snap
Mean concentration (mg/L)	19.1	19.2	41.8	42.6	8.3	8.3	35.7	35.5	46.2	46.4
% recovery of Snap Sampler		100.3		102.0		99.8		99.4		100.5
% RSD	0.7	0.4	0.5	1.3	0.3	0.1	0.2	0.6	0.8	0.6
72-hr	Control	Snap	Control	Snap	Control	Snap	Control	Snap	Control	Snap
Mean concentration (mg/L)	19.3	19.1	42.7	42.0	8.35	8.34	35.7	35.7	46.5	46.6
% recovery of Snap Sampler		99.0		98.5		99.9		100.0		100.0
% RSD	0.7	1.5	1.8	0.0	2.9	2.0	1.6	0.4	0.2	0.8

Table E2. Recovery of the anions in the second laboratory study.

Sample	Brom	ide	Chlo	ride	Nitrate		Perchi	orate	Sulfate	
24-hr	Control	Snap	Control	Snap	Control	Snap	Control	Snap	Control	Snap
Mean concentration (mg/L)	79.5	78.8	66.0	63.5	13.3	13.3	52.9	53.3	61.0	62.0
% recovery of Snap Sampler		99.1		96.2		100.0		100.8		102
% RSD	0.9	1.3	6.4	5.6	0.5	0.5	8.2	0.9	0.0	0.0
48-hr	Control	Snap	Control	Snap	Control	Snap	Control	Snap	Control	Snap
Mean concentration (mg/L)	80.0	80.5	64.0	68.5	13.3	13.4	49.7	52.7	61.5	63.0
% recovery of Snap Sampler		100.6		107		100.8		106		102
% RSD	0.0	0.9	0.0	9.3	0.5	0.5	0.4	3.2	1.1	2.2

72-hr	Control	Snap	Control	Snap	Control	Snap	Control	Snap	Control	Snap
Mean concentration (mg/L)	81.0	80.0	64.0	64.5	13.4	13.3	47.4	52.5	62.0	62.5
% recovery of Snap Sampler		98.8		100.8		99.6		111		100.8
% RSD	0.0	0.0	0.0	3.3	0.5	0.0	0.0	0.1	0.0	1.1

# Appendix F: Findings from Parker and Mulherin (2007)

Table F1. Summary of the findings for the Snap Sampler, exposed to a test solution containing VOCs<sup>1</sup>

Mean Concentration* (mg/L)							
Analyte	Control	Snap Sampler	Percent Difference				
tDCE	0.940	0.930	-1.1				
Benzene	0.994	0.989	-0.5				
TCE	0.970	0.965	-0.5				
Toluene	0.970	0.962	-0.9				
oDCB	1.02	1.01	-1.5				
mXYL	0.958	0.947	-1.2				
PCE	0.906	0.895	-1.2				

<sup>\*</sup> Mean of six replicate samples.

Table F2. Summary of the findings for the Snap Sampler, exposed to a test solution containing explosives<sup>1</sup>

Mean Concentration* (mg/L)							
Analyte	Control	Snap Sampler	Percent Difference				
HMX	0.682	0.704	3.2				
TNB	1.94	1.94	0.0				
RDX	5.93	5.92	-0.2				
1,3-DNB	0.133	0.132	-0.8				
TNT	1.40	1.39	-0.7				
2,4-DNT	0.104	0.104	0.0				

<sup>\*</sup> Mean of five replicate samples.

<sup>&</sup>lt;sup>1</sup> The Snap Samplers were equilibrated for 24 hours prior to sampling.

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Table F3. Summary of the findings from the holding-time studies for VOCs.

	Equili-	Equili- Mean Concentration (mg/L) <sup>1</sup>														
Holding time	bration	/ed?	ti	DCE	Ben	zene	т	CE	Tolu	uene	lo	OCB	m	XYL		PCE
(days)	Time (days)	Preserv	Control	SS												
7	1	No	0.235	0.242*	0.155	0.097*	0.235	0.231	0.131	0.05*	0.278	0.26*	< DL	< DL	0.177	0.166*
Percent diffe	erence			3.0		-38.0		-2.0		-61		-3.9				-6.1
7	3	No	0.417	0.435*	0.27	0.254	0.378	0.388*	0.191	0.172	0.328	0.328	0.111	0.008*	0.274	0.273
Percent diffe	erence			4.1		-0.7		2.8		-9.7		0		-93.0		-0.3
14	1	Yes	0.245	0.233*	0.206	0.205	0.245	0.230*	0.195	0.184*	0.298	0.271*	0.05	0.032*	0.192	0.162*
Percent diffe	erence			-4.6		-0.5		-5.9		-5.9		-8.9		-36.0		-16.0
14	3	Yes	0.591	0.599*	0.418	0.430*	0.536	0.539	0.309	0.298*	0.493	0.483*	0.243	0.187*	0.403	0.387*
Percent diffe	erence			1.5		2.9		0.5		-3.5		-2		-23.0		-3.8

<sup>&</sup>lt;sup>1</sup> Mean of 5 replicate samples.

<sup>\*</sup> Values with a statistically significant difference from control samples.

Table F4. Results from the holding-time study, using the explosives test solution (with 7-day holding time).

Analyte	Mean Conc (mg		Significant Difference?	Percent Difference
'	Control	Snap	Difference?	Difference
HMX	0.650	0.649	No <sup>1</sup>	
TNB	2.71	2.69	No <sup>2</sup>	
RDX	4.75	4.72	Yes <sup>1</sup>	0.63
1,3-DNB	0.212	0.215	No <sup>1</sup>	
TNT	0.976	0.970	Yes <sup>1</sup>	0.70
NB	0.116	0.115	Yes <sup>1</sup>	0.86
2,4-DNT	0.074	0.074	No <sup>1</sup>	

<sup>\*</sup> Mean of 5 replicate samples

<sup>&</sup>lt;sup>1</sup> Paired t-test

 $<sup>^{2}\,\</sup>mathrm{Wilcoxon}$  signed rank test

## REPORT DOCUMENTATION PAGE

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Approved for public release; distribution is unlimited.

#### 13. SUPPLEMENTARY NOTES

#### 14. ABSTRACT

Laboratory studies and a field demonstration were conducted to determine the ability of the Snap Sampler to recover representative concentrations of several types of inorganic analytes from ground water. Analytes included non-metals, transition metals, alkaline earth metals, alkali metals, and a metalloid. In the laboratory studies, concentrations of analytes in Snap Sampler samples were comparable with concentrations of the analytes in samples collected from a standpipe (i.e., control samples). For the field demonstration, there were sampling events at the former Pease Air Force Base. Samples taken using a Snap Sampler were compared with samples collected using conventional low-flow purging and sampling and a regenerated cellulose passive diffusion sampler. Based upon statistical analyses, analyte concentrations were found to be equivalent to those in the low-flow samples with one exception – unfiltered iron, where concentrations were significantly higher in the Snap Sampler samples. Differences were most pronounced in samples collected from the two stainless steel wells and from wells with higher turbidity levels. Elevated turbidities may have resulted from installing additional sampling equipment (including the baffle, pump, samplers, and bottom weight) in the well before sampling. We will examine this issue further at our next test site.

#### 15. SUBJECT TERMS

dialysis membrane sampler, equilibrated-grab sampler, low-flow purging and sampling, no-purge sampling, passive ground water sampling, passive sampling, regenerated cellulose sampler, Snap Sampler

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